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Modified Factor Analysis of Selected RAPS (Regional Air Pollution Study) Aerosol Data

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ABSTRACT

Target transformation factor analysis (TTFA) has been applied to an analysis of a subset of the aerosol-composition data acquired during the Regional Air Pollution Study (RAPS) for St. Louis, Missouri. The RAPS program collected a large number of samples with ten, continuously operated, dichotomous samplers from March 1975 to March 1977. The purpose of the present study was to evaluate the capability of TTFA to resolve sources of airborne particulate matter in a large set of ambient-aerosol samples. Only the samples from July and August 1976, both fine and coarse fractions, were examined in this study. To determine the most appropriate way to apply TTFA, two separate sets of the data were analyzed: 1) All the samples collected during the two months at a single station, and 2) All the samples collected during a single week at all ten RAPS stations. A more detailed source resolution was obtained when the data were further divided into subsets corresponding to the fine- and coarse-particle fractions. Because of the large number of different sources in the St. Louis area, superior results were obtained from the examination of the variation in aerosol composition with time at a single location rather than the spatial variation over multiple sites during a shorter time period.

CONTENTS

Abstract iii
Figures vi
Tables vii

1. Introduction 1

2. Conclusions 2

3. Recommendations 4

4. Background 6

5. Factor Analysis 8

6. Description of Data 15

7. Results For One Station 22

8. Results For One Week - All Stations 49

References 72
Appendix 76

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FIGURES

Number		Page
1.	Composition of the average sample in the fine and coarse fractions during July and August 1976 at RAPS station 112. Oxygen, nitrogen, and carbon constitute most of the mass not included in the data	19
2.	Mass concentration of the fireworks component for the six days around the Bicentennial Forth of July Celebration. The maximum potassium concentration on July 4th was 13,000 ng/m^3	29
3.	Average percent contribution of each source to the total average mass. The data are the fine- and coarse-fraction samples from RAPS station 112 for the months of July and August 1976	48
4.	A comparison of the calculated mass concentrations of the five source components at all RAPS stations. Both fine and coarse fractions are plotted at each station. These samples are from days Saturday, Sunday, and Monday	54
5.	A comparison of the calculated mass concentrations of the four source components in the fine-fraction data from all RAPS stations. These samples are from the week beginning July 31, 1976	64
6.	A comparison of the calculated mass concentrations of the five source components in the coarse-fraction data from all RAPS stations. These samples are from the week beginning July 31, 1976	65
7.	Average percent contribution of each source to the total average mass. The data are the fine- and coarse-fraction samples from all RAPS stations for the seven days beginning July 31, 1976	71

TABLES

Number		Page
1.	Summary of elements analyzed for RAPS station 112, July and August 1976	16
2.	Summary of elements analyzed for all RAPS stations, week beginning July 31, 1976	18
3.	Source profiles used as test vectors	20
4.	Results of dimensionality tests, RAPS station 112, July and August 1976, both size fractions	23
5.	Refined source profiles, RAPS station 112, July and August 1976, both size fractions	25
6.	Summary of mass contributions, RAPS station 112, July 1976, both size fractions	27
7.	Summary of mass contributions, RAPS station 112, August 1976, both size fractions	28
8.	Predicted vs. measured sample mass, RAPS station 112, July 1976, both fractions	30
9.	Predicted vs. measured sample mass, RAPS station 112, August 1976, both fractions	32
10.	Average mass contribution, RAPS station 112, both fine and coarse fractions	34
11.	Comparison of data with and without samples from July 4th and 5th, RAPS station 112, July and August 1976, both fractions	35
12.	Results of dimensionality tests, RAPS station 112, July and August 1976, fine and coarse fractions	37
13.	Refined source profiles, RAPS station 112, July and August 1976, fine fraction	38

14. Refined source profiles, RAPS station 112, July and August 1976, coarse fraction 39

15. Summary of mass contributions, RAPS station 112, July and August 1976, fine fraction, July 4th and 5th excluded 41

16. Summary of mass contributions, RAPS station 112, July and August 1976, fine fraction, July 4th and 5th included 42

17. Summary of mass contributions, RAPS station 112, July and August 1976, coarse fraction 43

18. Predicted vs. measured sample mass, RAPS station 112, July and August 1976, fine fraction 44

19. Predicted vs. measured sample mass, RAPS station 112, July and August 1976, coarse fraction 46

20. Results of dimensionality tests, all RAPS stations, one week, both fractions 50

21. Refined source profiles, all RAPS stations, SSM, both fractions 51

22. Summary of mass contributions, all RAPS stations, SSM, both fractions 53

23. Predicted vs. measured sample mass, all RAPS stations, SSM, both fractions 55

24. Average mass concentrations, all RAPS stations, SSM, both fractions 57

25. Results of dimensionality tests, all RAPS stations, one week, fine and coarse fractions 58

26. Refined source profiles, all RAPS stations, one week, fine and coarse fractions 60

27. Summary of mass contributions, all RAPS stations, one week, fine fraction 62

28. Summary of mass contributions, all RAPS stations, one week, coarse fraction 63

29. Predicted vs. measured sample mass, all RAPS stations, one week, fine fraction 67

30. Predicted vs. measured sample mass, all RAPS stations, one week, coarse fraction 69

SECTION 1

INTRODUCTION

In 1971, the first National Ambient Air Quality Standards were established, setting limits on permissible levels of total suspended particulate matter. Because these regulations concentrated only on the absolute amounts of suspended particulate matter, control efforts were directed primarily toward the removal of the larger, more massive particles that comprise most of the total mass of particle emissions. There is growing evidence, however, that the smaller particles, although representing a smaller fraction of the total mass, present the greater threat to public health and welfare. Because of their light scattering properties, the smaller particles also contribute to a larger extent to the reduction in visibility. Concern over the possible health effects of smaller-diameter particulate matter is reflected in the development and use of aerosol sampling equipment that measure the concentrations of particles in the inhalable (diameters less than 15μm) and and fine (diameters less than 2μm) particle-size fractions. New regulations, now under review by the EPA, may include standards not only on the mass of total suspended particles but on the levels of inhalable and fine particles as well. The effectiveness of regulations designed to limit the impact of fine and inhalable particles on the public would be greatly enhanced if the sources and relative emission rates of these particles were known. Determining the sources of airborne particulate matter is a very difficult problem because of the complexity of urban ecosystems. The problem is exacerbated by the presence of fugitive sources and the lack of understanding of the modes of formation and transport of airborne particles. The advent of receptor methodology and recent developments in the areas of trace-element analysis and multivariate statistical techniques now permit a much more detailed analysis of ambient aerosol samples. By providing detailed information on the sources of fine and inhalable particles, such techniques could become a major part of any strategy for controlling airborne particulate matter.

SECTION 2

CONCLUSIONS

1. Target transformation factor analysis (TTFA) can be used to resolve sources of airborne particulate matter from large sets of ambient aerosol samples. With this method, the contribution of each source to each sample can be calculated. In addition, TTFA requires no a priori assumptions as to the number or nature of the sources in the system. This method could be an important tool in the achievement of mandated limits on suspended particulate matter in the urban areas of this country by identifying those sources where imposition of control technolgy would be the most cost-effective approach.

2. TTFA can resolve strong sources that are present in only a few of the samples and a source-profile vector for the source can be predicted from the data. Other methods for performing quantitative source resolutions cannot account for such sources unless their presence is initially known and a measurement of the source composition is available.

3. The presence of several samples with one very strong source was found to conceal the presence of other, weaker, factors in the full data set. Removal of the affected samples permitted the resolution of additional sources.

4. Source profiles of coal-burning power plant emissions may be identified by TTFA. Distinguishing crustal material from flyash would be more certain if reliable data for additional elements that help differentiate these two sources were available.

5. TTFA can resolve sources with dependence on the same element such as lead in particles from motor vehicle exhaust and lead and/or zinc smelters.

6. The analysis of the July and August data from one RAPS station produced a reasonable source resolution. The data from one week at all RAPS stations seem to be composed from a number of sources that are significantly different at each station. The large number of sources contributing to the ten RAPS stations precluded the resolution of any but the most important sources.

7. By dividing both data sets into fine- and coarse-fraction subsets, additional sources were resolved, indicating that the sources contribute primarily to either the fine or coarse fractions, but not both.

8. During July and August 1976, the major contributor to the fine-fraction samples from station 112 was the secondary sulfate aerosol, representing about 64% of the average sample. Motor vehicle emissions account for 15% and soil or flyash for about 11%. For the coarse fraction, the two crustal components, soil and limestone, account for about 80% of the average sample with sulfate contributing about 12%.

SECTION 3

RECOMMENDATIONS

With some additional development, target transformation factor analysis could be a valuable tool in the efforts of local authorities to devise cost-effective strategies for the control of airborne particulate matter. To insure the credibility of any sort of statistical analysis, it is important that there be some indication of the reliability of the calculated results. In the present study, the actual nature of the sources were not known so the accuracy of the quantitative results could not be determined. Testing, under more controlled conditions, is essential to insure that the calculated results are both accurate and reliable. One way to evaluate the accuracy of this method would be to analyze computer-generated data sets containing randomly generated errors that approximate typical analytical uncertainties and source-composition variability. Comparison of the starting data with the calculated results would give an indication of the reliability of the analysis. Another way to verify the quantitative results would be to analyze samples prepared in the lab from known amounts of well-characterized materials. Comparison of the calculated results with the known concentration of each sample would determine the quality of the source resolution. A third, and more complex, way to verify the quantitative results would be to compare the results of the factor analysis of real samples with results obtained by x-ray diffraction and/or microscopic examinations of the same samples.

Further development of target transformation factor analysis would include error models to give a better indication of the reliability of the calculated source profiles and to provide limits on the uncertainties of the calculated contributions of each factor. In addition, more objective and explicit criteria for determining the number of correct factors to be retained are needed. The analyses of computer-generated data sets could shed additional light on the still nebulous process of determining the number of factors.

Performing a source resolution of ambient aerosol samples requires a complete and accurate data set. If all the sources that contribute to a system are to be resolved, it is important that the data set include as many elements as possible. In the present study, the measured elements accounted for less than half of the total measured mass of each sample. The inclusion of other elements such as carbon and other gaseous species such as SO_2 would have greatly facilitated the analyses. In addition, the exclusion of the element arsenic because of the large number of determinations below the detection limits, inhibited the resolution of a factor for coal flyash.

Future air quality studies should attempt to produce accurate data for both the total level of suspended particulate matter and as many elements and chemical species as practical.

SECTION 4

BACKGROUND

One approach to the problem of determining the contribution of each source to the total level of suspended particulate matter is the method of source-emissions inventories and atmospheric dispersion models. Using estimated emission rates for all known sources along with a model for their behavior following emission, this method attempts to determine the contribution of each source to the total aerosol concentration. The results of source-emissions inventories are too often unsatisfactory due to a lack of accurate source-emission profiles and the inability to include fugitive sources. The development of improved aerosol sampling equipment permitted the development of receptor methods for the determination of source contributions. These methods employ statistical analysis techniques to calculate the contribution of each source of particulate matter from a representative set of ambient aerosol samples. Receptor methods have primarily taken the form of the chemical element balance (CEB) method first developed by Miller, Friedlander, and Hidy (1). In this method, it is assumed that the number and composition of the sources are known. The observed elemental concentrations in a set of ambient aerosol samples are fit by means of a regression analysis. Early applications of the chemical element balance were to ambient aerosol samples from Pasadena, California (1), Ghent, Belgium (2), Heidelberg, Germany (3), and Chicago, Illinois (4). These early applications of the chemical element balance method suffered from a lack of reliable data for the source emission profiles needed for the analysis. Recent improvements in the quality of source profile determinations (5-9) have produced good agreement between the calculated and measured elemental concentrations for airborne particulate matter in Washington, D.C. (10) and for dichotomous sampler data in St. Louis and the Great Smokey Mountains (11). The scope of the chemical element balance method was further expanded in an extensive study of the Portland, Oregon aerosol as part of the PACS program (12,13). This study included components such as vegetative and grass burning and chemical species such as volatile and non-volatile carbon, nitrate, and sulfate that had not previously been used. By including the larger number of source components, very good agreement with the measured concentrations was achieved for the 23 elements and chemical species that were included in the analysis. Chemical element balance methods have a major drawback in that they require an *a priori* knowledge of both the number and composition of the suspected source emissions. The only quantities calculated are the contribution of each of the presumed sources to each of the measured samples. Though extensive efforts by the groups in Maryland and Oregon have produced much better determinations of

the elemental profiles of a number of sources, these determinations are time consuming, expensive, and, in many cases, inapplicable to the resolution of aerosol sources in different locations. In addition, source determinations of in-stack material cannot account for chemical and physical transformations of volatile species following emission.

Multivariate statistical techniques, including factor and cluster analyses, represent a different approach to aerosol source resolution. A major advantage of these methods is that they require no prior assumption about the nature of the system under study. In an early application of multivariate statistical techniques to elemental source resolution, Hopke, et al. (14) used factor and cluster analyses to identify sources of airborne particulate matter in the Boston urban aerosol. In this study, the data were first transformed into a standardized form that removed the effects of using different metrics in describing the data. The identification of sources was made by associating the largest calculated factor loading with the marker element for each source. In a similar fashion, factor and cluster analyses were used to characterize the aerosol of Tucson, Arizona (15). Gatz (16) used factor analysis to identify sources of particulate matter in St. Louis. Factor analysis of a matrix of standardized variables resolves only the variance in the system, not the actual data values. In addition, the calculated factor scores provide only a measure of the relative importance of each source rather than the actual amount of contributed material.

Several recent studies (17-21) have employed a new form of factor analysis called target transformation factor analysis (TTFA). Originally developed by Malinowski and co-workers (22), this technique permits an analysis, similar in nature to the chemical element balance method, but without the presumptions as to the number or nature of the sources in the system. Unlike the prior applications of factor analysis, TTFA allows the investigator to use his understanding of the system to determine the best representation of the actual source concentration profiles. TTFA also permits the direct calculation of the contribution of each source to each sample. By providing reliable quantitative source resolutions, without the need for advance detailed knowledge of the nature of the particular system, target transformation factor analysis could be an important tool in the future achievement of mandated TSP levels.

SECTION 5

FACTOR ANALYSIS

Performing a source resolution by factor analysis requires a set of n ambient aerosol samples that have determinations for m individual elements. The maximum size of m and n is limited only by the amount of available computer space, but both must be at least as large as the number of sources contributing to the system.

In a factor analysis, it is assumed that each datum point can be represented by a sum of the contributions from each of the distinct sources that comprise the system. Algebraically, this model is of the form

$$x_{ij} = a_{i1}f_{1j} + a_{i2}f_{2j} + \cdots + a_{ip}f_{pj} \qquad (1)$$

where x_{ij} denotes* the amount of element i in sample j and p is the number of sources in the system. In equation 1, the contribution from each source is expressed as a product of two cofactors, a_{ik} and f_{kj}. The former represents the concentration of the ith element in particles emitted by the kth source while the latter is the amount of particulate matter per unit volume contributed by source k to sample j. The sum of the contributions from the p sources is the total amount of the element per unit volume observed in a sample. Because of the nature of the factor model in equation 1, only variables that are linearly additive properties of the system can be included in the data. The entire data set can be resolved into source contributions given by the matrix equation

$$X = AF \qquad (2)$$

where A is a matrix of dimension m x p containing the concentration-profile vectors for each of the p sources and F, a p x n matrix, is the amounts per unit volume that each source contributes to each sample. The objectives of a factor analysis are 1) To determine p, the number of independent sources that contribute to the system, 2) To determine the components of matrix A, the

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*Lower case letters will be used to denote an element of a matrix while upper case letters will denote a complete matrix.

elemental-source profiles, and 3) To calculate F, the contribution of each source to each sample.

In the early applications of factor analysis (14-16), the data were first transformed into a standardized form given by

$$z_{ij} = \frac{x_{ij} - \bar{x}_i}{\sigma_i}$$

where z_{ij} is the standardized value of the ith element for the jth sample, $\bar{x}_i$ is the mean value for the ith element, and σ_i is the standard deviation of the distribution of the values of the element. Each standardized variable has a mean value of zero and a standard deviation of one. For a matrix of standardized variables, the factor model of equation 2 becomes

$$Z = AF$$

Factor analysis of a matrix of standardized variables attempts to linearly apportion the variance among the different factors. The use of standardized variables permits the inclusion in the data matrix, X, of variables other than elemental concentrations, e.g. particle size and density, or wind direction.

The initial step in a factor analysis is to transform the data into a correlation matrix that provides a measure of the pairwise interrelationship between either the elements or samples. In the terminology of Rozett and Petersen (23), a correlation between elements is called an R analysis while a correlation between samples is called a Q analysis. The early applications of factor analysis used the matrix of correlations between elements given by

$$C = ZZ^t$$

A correlation between elements (R analysis) normalizes the data for each element, destroying any information about the relative elemental concentration in each sample. A Q analysis preserves this information by normalizing the data for each sample. Rozett and Petersen (23) compared the two methods and determined that the correlation between the samples retains the more significant information and it is this matrix that has been used in the present study.

The correlation about the origin between samples is given by

$$C = (XV)^t(XV) \qquad (3)$$

where V is a diagonal matrix with elements defined by

$$v_{jj} = \left(\sum_{i=1}^{m} (x_{ij})^2 \right)^{-1/2}$$

Here the lower case t denotes the transpose matrix.

The correlation matrix, given by equation 3, is next diagonalized by finding a matrix Q such that

$$Q^{-1}CQ = \Lambda \tag{4}$$

where Λ is a diagonal matrix of eigenvalues arranged in decreasing order of magnitude and Q contains the associated eigenvectors that span the data space. For non-equal eigenvalues, the eigenvectors will be orthogonal since C is a symmetric matrix. Thus

$$Q^t = Q^{-1} \tag{5}$$

Combining equations 3, 4, and 5 yields

$$Q^t(XV)^t(XV)Q = \Lambda \tag{6}$$

If matrix A is now defined to be

$$A = XVQ \tag{7}$$

then a comparison of equations 2 and 7 leads to the following definition for matrix F

$$F = Q^tV^{-1} \tag{8}$$

Thus, the data have been factored into the product of two matrices, A and F, defined by equations 7 and 8, respectively. The product of matrices A and F is exactly X.

In theory, p, the number of sources in the system, is equal to the number of non-zero eigenvalues obtained from the diagonalization. The remaining n-p eigenvalues should be equal to zero and can be excluded from the analysis since they contribute no information. In practice, however, the presence of sampling, analytical, and calculative errors makes the determination of the proper number of factors difficult. Several different tests to aid in the determination of the dimensionality of the data have been developed. A large decrease in the magnitude of successive eigenvalues resulting from equation 4 is one indicator of the correct number of factors. In another test, the data are reproduced with only the first factor and compared point-by-point with the original data. An average error, chi-square, and Exner value are calculated. The Exner function (24) is defined by

$$E^p = \left(\frac{\sum_{i,j} (x_{ij} - x_{ij}^p)^2}{\sum_{ij} (x^0 - x_{ij}^p)^2} \right)^{-1/2}$$

where x_{ij} is an original datum point, x'_{ij} is the point reproduced with p retained factors, and $\bar{x}$ is the grand mean of the experimental data. Close agreement between the reproduced and original matrix is indicated by an Exner value of zero. The data are next reproduced with both the first and second factors and again compared point-by-point with the original data. This procedure is repeated, each time with one additional factor, until the data are reproduced with the desired precision and the inclusion of additional factor does not significantly improve the fit. If p is the minimum number of factors needed to adequately reproduce the data, then the remaining n-p factors can be eliminated from the analysis. In this manner the dimension of the A and F matrices is reduced from n to p. The dimensionality tests rarely provide unequivocal indicators of the number of factors that should be retained. Some judgement becomes necessary in evaluating all of the test results and deciding upon a value for p.

The factors produced by the diagonalization of the correlation matrix are generally not interpretable in terms of physically real source-element profiles. In order to relate the abstract factor matrix to one with physical significance, it is necessary to geometrically realign the factor axes of the A matrix with axes that are interpretable in terms of real concentration profiles. In the previous applications of factor analysis to element-source identification studies (14,15), the matrix of factors was rotated in such a way so as to maximize the number of values that are either zero or unity. This rotation criterion, called "simple structure" (25) is not very useful for environmental source resolution since an element may be emitted by several sources and thus the values should not be limited to either zero or unity, but rather something in between.

A different approach to axis rotation has been developed by Malinowski (22) that permits the investigator to use his understanding of the system to suggest the nature of factors. This procedure, called target transformation, involves testing a set of input source profiles to determine the degree of overlap with the data. The input source profiles, called test vectors, are derived from existing knowledge of the measured elemental composition of actual source materials. In the case of an aerosol source resolution, possible test vectors would include the profile of elements emitted by sources such as automobiles, volcanoes, coal-fired or oil-fired power plants, soil, sea salt, municipal incinerators, etc. The target transformation procedure utilizes a rotation matrix R. Rewriting equation 2

$$X = ARR^{-1}F \tag{9}$$

It can be shown (see appendix) that for test vector b, the rotation vector, r, in matrix R, is given by

$$r = \Lambda^{-1}A^{t}b \tag{10}$$

Each rotation vector aligns a column of A with an input test vector so as to

maximize the least squares overlap between one column of the rotated A matrix and b, the test vector. The degree of alignment between the test vector and the rotated column of A determines if b is a good representation of one of the sources in the data. In addition to source profile test vectors, uniqueness test vectors that have all but one element set equal to zero are analyzed for all elements. An element is considered unique if its concentration in the data is de-coupled from all other elements. The uniqueness test also determines if the concentration of one element is strongly related to any other elements. The test vector predicted by the uniqueness test can then be used as a normalized source concentration profile for sources whose concentration profiles have not been measured. The target transformation rotation given by equation 10 is dominated by the more abundant elements in the data. In order to resolve sources with similar elemental profiles, it is important that all elements have equal weight in the rotation since it is often the variation in the concentration of some trace elements that permit differentiation of sources with similar major-element compositions. A weighted target transformation scheme has been added to our computer program and has greatly enhanced the ability of the analysis to resolve sources with similar concentration profiles. For a weighted least-squares rotation, the quantity to be minimized is (26)

$$\varepsilon^2 = (Ar - b)^t W(Ar - b)$$

The derivation is similar to that for the unweighted rotation given in the appendix. For the weighted target transformation, the rotation vector for a test vector, b, is given by

$$r = (A^t WA)^{-1} A^t Wb$$

where W, the weight matrix, is a diagonal matrix consisting of the inverse of the variance of the distribution of each element. The variance for each element is calculated from (27)

$$\sigma_i^2 = \frac{1}{n-1} \sum_{j=1}^{n} (x_{ij} - \bar{x}_i)^2$$

where σ_i^2 is the variance of the distribution for element i, $\bar{x}_i$ is the mean value for element i calculated from (27)

$$\bar{x}_i = \frac{\sum_{j=1}^{n} x_{ij}/\sigma_{ij}}{\sum_{j=1}^{n} 1/\sigma_{ij}}$$

and x_{ij} and σ_{ij} are the experimentally determined concentration and error for each datum point.

Once a test vector has been identified as a possible source, it can be refined by replacing the input value for a given element with the value predicted by the target transformation. Thus, since we expect differences between the elemental emissions profiles of similar sources or even the same source at different times, the target transformation procedure provides a feedback mechanism whereby the concentration profiles can be directed by the analysis toward the best possible fit. In addition, where an element has undergone a chemical or physical transformation after emission, the source profiles are modified to reflect the change.

When a number of possible sources have been identified, they are combined p at a time to form B, a matrix of test vectors, and R, a matrix of their corresponding rotation vectors. Substituting B for the rotated A matrix, AR, and calculating a new F matrix from

$$\bar{F} = R^{-1}F \tag{11}$$

lead to

$$\bar{X} = B\bar{F}$$

where $\bar{X}$ is the data reproduced with the chosen set of test vectors given by matrix B. The original data are compared point-by-point with $\bar{X}$ to determine how well the chosen set of test vectors represent the actual sources in the data. This comparison can also suggest further refinements to the test vectors that might improve the overall agreement. Repetition of the calculation of X with different combinations of test vectors allows the best possible set of source profiles to be determined.

A computer program (28), based on a program developed by Malinowski and coworkers (29), has been written to perform the factor analysis. Including the addition of the weighted target transformation, a number of other modifications have been made in the course of this study. One major change now permits the lengthy matrix diagonalization procedure to be performed only once, thus greatly reducing the calculation time for each analysis.

The absolute concentrations of the measured source profiles may not correspond exactly to those found in the area under study. Therefore, before the selected set of test vectors can be used to calculate the mass contribution of each source to each sample, they must be scaled to reflect the actual concentration of each element in the source material. In addition, the source vectors developed from the uniqueness test are usually scaled to a maximum concentration of unity. Correct scaling factors for all source profiles can be determined from the calculated source contributions and the total measured sample weights by means of a multiple regression analysis of the form

$$m_j = \sum_{k=1}^{p} \frac{\bar{f}_{kj}}{s_k} \qquad j=1,n \qquad (12)$$

Where m_j is the measured mass of sample j, $\bar{f}_{kj}$ is the mass matrix calculated in equation 11, and s_k are the scaling factors to be calculated by the regression analysis. Comparison of the predicted and measured sample masses gives another indication of the quality of the fit with the selected set of test vectors. Occasionally, a scaling factor will produce an elemental concentration in one factor of over 100%, indicative of a very weak source that has not been well resolved by the factor analysis. In the absence of data for the masses of the samples, scaling factors must be estimated based on values found in the literature or on the stoichiometry of the anticipated chemical compounds.

SECTION 6

DESCRIPTION OF DATA

The data used in this study were produced as part of the Regional Air Pollution Study (RAPS) for St. Louis, Missouri. In the RAPS program, automated dichotomous samplers were operated over a two year period at ten sites in the St. Louis metropolitan area. Ambient aerosol samples were collected in fine, <2.4μm, and coarse, 2.4 to 20μm, fractions (30). Samples were analyzed at the Lawrence Berkeley Laboratory for total mass by beta-gauge measurements and for twenty-seven elements by x-ray fluorescence (31). For the present study, a computer tape containing only the data for the the months of July and August 1976 was obtained from the Environmental Sciences Research Laboratory, Research Triangle Park, NC.

To determine the most appropriate way to apply target transformation factor analysis to a large set of aerosol samples, two subsets of this data were analyzed: 1) All the samples collected during July and August at one station and 2) The samples collected during a single week at all ten RAPS stations. The data from station 112 were selected for the first subset and the week beginning July 31, 1976 for the second. The relative completeness of the data in these two subsets was the primary criterion for their selection.

Station 112 was located near Washington University, west of downtown St. Louis. During the sixty-two days of July and August, filters were changed at twelve hour intervals producing a total of 124 samples in each the fine and coarse fractions. Data were missing for forty-eight of the samples leaving a total of 200. Of the twenty-seven elements determined for each sample, a majority of the determinations of ten elements were below the detection limits. Since a complete and accurate data set is required to perform a factor analysis, these ten elements were eliminated from the analysis. Table 1 lists the full twenty-seven elements and the number of values below detection limits. Note that the element arsenic was excluded because of the large number of determinations below detection limits. Arsenic determinations by x-ray fluorescence are often unreliable because of an interference between the arsenic K x-ray and the Lead L x-ray. A neutron activation analysis of these samples should produce better arsenic determinations. Reliable data for arsenic may be important to the differentiation of coal flyash and crustal material; two materials with very similar source profiles. Because of limitations in available computer space, the remaining 200 samples were analyzed in two separate parts. Two different divisions in the data were made to determine which permitted the extraction of the most information.

Table 1.

RAPS Station 112, July and August 1976

Element	Number of Values Below Detection Limits
Al	15
Si	2
P*	179
S	0
Cl	35
K	0
Ca	0
Ti	39
V*	162
Cr*	151
Mn	29
Fe	0
Ni	95
Cu	39
Zn	0
Ga*	194
As*	196
Se	113
Br	1
Rb*	130
Sr	73
Cd*	161
Sn*	160
Sb*	180
Ba	131
Hg*	196
Pb	0

*Elements excluded from the analyses.

Separate analyses were then performed on each group. First, the data were divided into groups corresponding approximately to the months of July and August. In the second analysis, the data were divided into groups corresponding to the fine and coarse fractions of both months.

During the week beginning July 31, 1976, filters were changed at twelve hour intervals at five of the stations and at six hour intervals at four stations. Data from station 120 were not included in the version of the tape supplied by EPA. A total of 182 samples were collected in each the fine and coarse fractions. Data were missing for forty-three samples and another fifty samples had a majority of determinations below the detection limits; these ninety-three samples were excluded from the analysis. Of the twenty-seven elements, a majority of the determinations of twelve had values below detection limits. These twelve elements were excluded. Table 2 lists the number of values below detection limits in the data for one week. Again, two separate divisions in the data were made and each individually analyzed. The data were first divided into two groups composed of days Saturday, Sunday, and Monday (SSM), and of days Tuesday, Wednesday, Thursday, and Friday (TWTF). The first group, with 115 samples, corresponds to days 213, 214, and 215, and the second group, with 156 samples, to days 216 through 219. The analysis was then repeated with the data divided into groups corresponding to the fine and coarse fractions with 139 and 132 samples respectively.

The twenty-seven elements determined for each sample account for only a small fraction of the total sample mass. Figure 1 depicts the composition of the average sample in both the fine and coarse fractions at RAPS station 112. The measured elements account for only about 22% of the average sample mass in the fine fraction and about 43% in the coarse. The remaining mass consists primarily of oxygen, nitrogen, and carbon. Determining the sources of particulate carbon is of growing concern because of the potential mutagenicity associated with carbonaceous particles (32,33). Measurements have shown that both soot and organic carbon can account for a sizable fraction of the total mass of airborne particulate matter. Lewis and Macias (34) measured a carbon concentration of 16% in the fine fraction in Charleston, West Virginia. A carbon concentration of 37% was reported for Portland, Oregon (13). Radiocarbon studies have determined that over 80% of the particulate carbon in the St. Louis aerosol is of fossil-fuel origin (35,36). Though no measurements of carbon are included in the RAPS data, that portion of the sample mass must be accounted for by the other sources. This can often lead to distortions in the scaling factors produced by the multiple regression analysis. In order to produce the best possible source resolutions, it is vital to have both accurate TSP measurements and determinations for as many elements as possible.

For use in the target transformation portion of the analysis as test vectors, a set of seventeen potential source profiles was assembled from the literature. These seventeen include nine different crustal factors (1,9,37-41), two determinations of coal flyash (5,42), three automobile factors (8,11,39), and three industrial sources (cement (39), paint (11), and steel (11)). The seventeen test vectors are listed in Table 3.

Table 2.

One Week Beginning July 31, 1976.

All RAPS Stations

Element	Number of Values Below Detection Limits
Al	135
Si	27
P*	265
S	16
Cl	115
K	0
Ti	170
Ca	1
V*	318
Cr*	288
Mn	149
Fe	1
Ni*	267
Cu	120
Zn	18
Ga*	321
As*	316
Se	201
Br	0
Rb*	294
Sr*	224
Cd*	273
Sn*	258
Sb*	309
Ba	291
Hg*	320
Pb	3

*Elements excluded from the analyses.

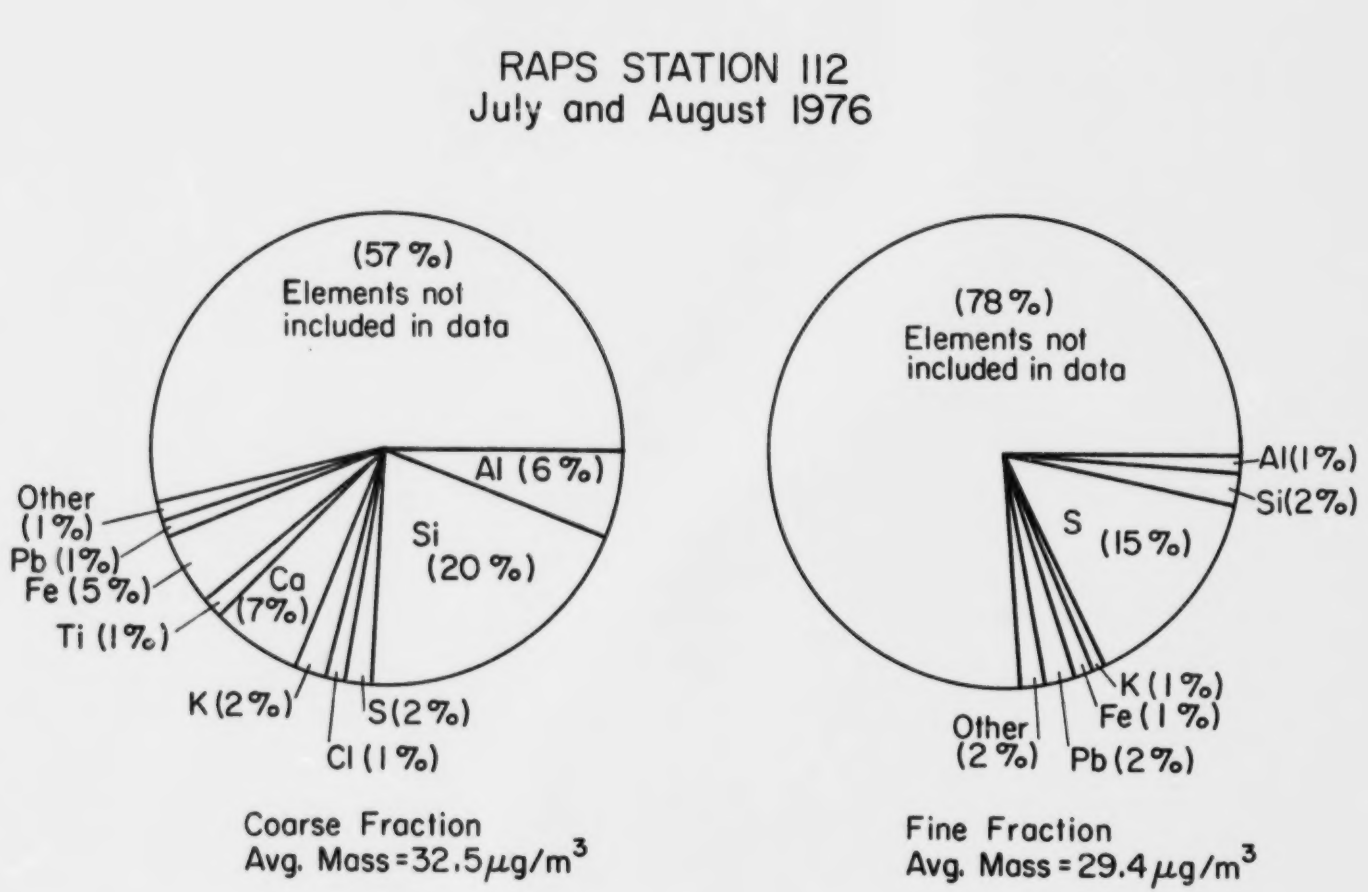

Figure 1. Composition of the average sample in the fine and coarse fractions during July and August 1976 at RAPS station 112. Oxygen, nitrogen, and carbon constitute most of the mass not included in the data.

Table 3. Source Profiles Used as Test Vectors. (mg/g)

Element	Soils								
	Shale(37)*	Sandstone(37)	Carbonate(37)	IAEA(38)	Soil 1(39)	Soil 2(1)	Soil 3(40)	Rock(41)	Soil 4(9)
Al	80	25	4.2	82	82	69	71	82	60
Si	273	368	24	332	200	260	330	282	350
P	0.7	0.17	0.4	1			0.8	1.1	
S	2.4	0.24	1.2				0.85	0.26	
Cl	0.18	0.01	0.15				0.1	0.13	
K	26.6	10.7	2.7	19	15	25	13.6	20.9	
Ca	22.1	39.1	302	22	15	10	13.7	41.5	
Ti	4.6	1.5	0.4	5	4	3	4.6	5.7	
V	0.13	0.02	0.02	0.15	0.06	0.04	0.1	0.14	0.14
Cr	0.09	0.035	0.011	.03			0.2	0.1	0.06
Mn	0.85	10	1.1	15	1.1	0.6	0.85	0.95	0.99
Fe	47.2	9.8	3.8	45	32	20	38	56.3	37.8
Ni	0.068	0.002	0.02	0.013	0.04	0.02	0.04	0.075	
Cu	0.045	0.001	0.004	0.077	0.08	0.02	0.02	0.055	
Zn	0.095	0.016	0.02	0.4			0.05	0.07	0.08
Ga	0.02	0.02	0.004	0.02			0.03	.015	
As	0.013	0.001	0.001	0.09			0.005	0.002	0.005
Se	0.0006	0.00005	0.00008	0.001			0.00001	0.00005	0.0006
Br	0.004	0.001	0.0062	0.005			0.005	0.003	
Rb	0.14	0.06	0.003	0.14			0.1	0.09	
Sr	0.3	0.002	0.61	0.33			0.3	0.4	
Cd	0.0003			0.0015				0.002	
Sn	0.006							0.002	
Sb	0.0015		0.0002	0.56				0.0002	0.0006
Ba	0.58	0.01	0.01	0.6	0.6	1	0.5	0.43	
Hg	0.0004			0.001				0.0001	
Pb	0.02	0.007	0.009	0.13	0.2	0.06	0.01	0.013	

Continued

*Numbers in parentheses refer to full reference list.

Table 3. Continued

Element	Flyash		Motor Vehicles			Industrial		
	NBS(42)	Gladney(5)	Auto 1(8)*	Auto 2(11)	Auto 3(39)	Cement(39)	Paint(11)	Steel(11)
Al	127	133				24		11
Si	210	208				107		7
P				0.9				1
S				6				
Cl	0.042		0.1	19	68			
K	16.1	13.6				5.3		
Ca	47	10.6	0.054			460		12
Ti	7.4	8.1				1.4	422	
V	0.24	0.26						
Cr	0.13	0.19						
Mn	0.5	0.39						
Fe	62	123		0.6				
Ni	0.16	0.0006	0.05	1	4	11	4	31
Cu			0.005				204	570
Zn	0.2	0.23	0.01					
Ga		0.078		3	1.4			
As	0.058	0.16						
Se	0.01	0.025	0.0005					
Br	0.012	0.006	0.38					
Rb	0.13	0.11		37	79			
Sr	1.7	0.81						
Cd			0.002					
Sn								
Sb	0.007	0.006	0.0008					
Ba	2.7	1.14	0.013					
Hg				0.9				
Pb	0.075	0.056	1	148	400			

*Normalized to Pb = 1.0

SECTION 7

RESULTS FOR ONE STATION

Analyses of the data from RAPS station 112 were performed using both the weighted and unweighted form of the target transformation. The basic source profiles produced by both rotation schemes were not significantly different. Both could fit the major elements in each data set fairly well. The weighted form of the rotation, because it gives more equal weight to all the elements, produced better fits for both major and trace elements. Only the results using the weighted form of the target transformation are reported here.

DATA DIVIDED BY MONTHS

The first step in the analysis is to determine the minimum number of factors needed to represent the data. The results of the tests that aid this determination are given in Table 4. For the July data, the large change in the magnitude of the eigenvalues at five retained factors combined with the low chi-square and Exner values, indicates that this is the best number of factors to represent the data. The test results for the August data were less conclusive, indicating the possibility of either five, six, or seven factors. In such cases, parallel analyses with all possible number of factors are performed to determine the best fit to the data. The computer program we have prepared is set up to handle simultaneously such parallel analyses.

In the target transformation portion of the analysis, the seventeen source profiles and uniqueness test vectors for all elements were analyzed to determine the degree of overlap with any of the calculated factor axes. For the July data, the uniqueness test vector for potassium identified a source strongly related to potassium but containing Al, Cl, Zn, Sr, and Ba as well. This factor is attributed to the presence of fireworks particles resulting from the July 4th Bicentennial display near station 112. Fireworks particles were found to impact three samples from July 4th and 5th in the fine fraction and one sample from July 4th in the coarse fraction. The resolution of a fireworks factor, though significant in only three of the one hundred samples, illustrates the source resolution power of this method. The uniqueness test vectors for the elements lead and sulfur were also found to agree fairly closely with the July data. The concentration of lead was found to be related to that of bromine; usually indicative of a motor vehicle source. The concentration of sulfur was not related to any other elements and probably

Table 4. Results of Dimensionality Tests

RAPS Station 112, July and August 1976

July, 1976

Factor	Eigenvalue	Chi Square	Exner	Average % Error
1	61.5	1700	.6851	220
2	34.5	175	.2221	100
3	1.4	154	.1791	100
4	1.3	475	.1295	100
5	1.0	50	.0635	69
6	.2	44	.0443	60
7	.08	42	.0304	56
8	.04	129	.0198	56
9	.01	64	.0144	43

August, 1976

Factor	Eigenvalue	Chi Square	Exner	Average % Error
1	58.	1300	.7173	307
2	39.	130	.1895	130
3	1.5	68	.1341	100
4	.8	69	.0906	96
5	.3	68	.0697	71
6	.2	66	.0592	69
7	.1	40	.0324	61
8	.03	38	.0256	53
9	.02	36	.0188	43

represents a secondary sulfate aerosol resulting from primary sulfur oxide emissions. The uniqueness test for July also indicated the presence of two crustal sources, one, an alumino-silicate type and the other of limestone or cement origin. In an earlier factor analytical study of aerosol sources in the St. Louis area, Gatz (16) found the element calcium to be associated with other than crustal sources. The high calcium loading at one site was attributed to cement plants in the sampling area. Kowalczyk (10) reports finding potassium to calcium ratios of 0.8 in plume aerosols collected over a cement plant near Washington, D.C. The uniqueness test for calcium shows no strong correlation between calcium and potassium, indicating the origins of the source are probably crustal. Based on their degree of alignment with the data, a motor vehicle source, two crustal sources, soil and limestone, were selected from the set of input source determinations. Since the fireworks and sulfate sources had no prior source determinations, the source vectors predicted by the uniquenss test were used for these source profiles. The five source profiles were then refined by replacing the original values for each element with the values predicted by the target transformation.

For the August data, the silicon, sulfur, calcium, and lead results were similar to those obtained for the July data and there was no fireworks factor. However, when five factors are retained, a unique factor for titanium is found. The uniqueness test associated the concentration of titanium with the element iron. Rheingrover (43) identified the source of titanium as a paint-pigment factory located to the south of station 112. From the set of test profiles, there was good agreement for only four sources: Soil, limestone, motor vehicles, and paint pigment. These four and the sulfate factor were the only sources that could be resolved in the August data. In neither the July nor August data was a factor for coal flyash resolved. It would be expected for flyash to be an important source of airborne particulate matter in the St. Louis area but differentiating flyash from crustal material is a problem often encountered in studies of urban aerosols.

Scaling factors for all source profiles were determined from the calculated source contributions and the total measured sample weights by means of the multiple regression analysis (equation 12). The scaled source profiles that best reproduced the July and August data are listed in Table 5. The calculated profiles of the two crustal components follow the shale and limestone element profiles of Mason (37). The low aluminum concentration in the July limestone profile is probably due to the contribution of the fireworks component that is significant in only a few samples but is included in the whole analysis. The sulfur concentration in the sulfate factors are consistent with that of ammonium sulfate. Lewis and Macias (34) suggest that ammonium sulfate is the main chemical form of both sulfur and nitrogen in fine-fraction particles. In his study of the RAPS data, Dzubay (11) assumed that sulfur was present in the form of ammonium sulfate in both the fine and coarse fractions. The calculated lead concentrations in the motor vehicle components of eight and nine percent with a lead to bromine ratio of about 0.25 are typical of values reported in the literature (44). The concentration of lead in motor vehicle exhaust will vary from city to city and is dependent on the ratio of leaded gasoline to unleaded and diesel-powered vehicles. In the paint-pigment component, the titanium and iron concentrations are similar

Table 5. Refined Source Profiles. (mg/g)

RAPS Station 112

July 1976, Both Fractions

Element	Sulfate	Motor Vehicle	Soil	Limestone	Fireworks
Al	2.1	11.	76.	0.0	54.
Si	2.5	2.8	240.	75.	7.
S	240.	3.2	2.	2.7	46.
Cl	1.7	1.0	1.6	25.	13.
K	1.	0.0	16.	13.	435.
Ca	0.0	2.4	31.	230.	0.5
Ti	1.2	2.6	1.7	35.	0.0
Mn	0.45	0.22	0.74	2.4	1.3
Fe	4.9	6.3	42.	38.	6.5
Ni	0.046	0.11	0.063	0.12	0.12
Cu	0.3	0.6	0.01	0.9	1.9
Zn	2.8	1.4	0.0	5.9	6.6
Se	0.12	0.06	0.003	0.08	0.0
Br	0.0	20.	0.6	0.6	3.2
Sr	0.0	0.0	0.2	0.4	9.
Ba	0.3	0.7	0.3	2.2	11.
Pb	7.1	78.	1.4	2.4	2.1

August 1976, Both Fractions

Element	Motor Vehicle	Soil	Limestone	Paint	Sulfate
Al	3.5	53.	53.	17.	1.2
Si	0.0	220.	27.	0.0	0.8
S	0.0	8.	0.0	0.0	230.
Cl	5.6	3.5	39.	11.	1.3
K	13.	18.	0.5	20.	0.9
Ca	0.0	55.	300.	17.	0.5
Ti	0.0	2.2	11.	140.	1.1
Mn	2.2	1.2	0.5	7.2	0.0
Fe	4.	41.	52.	135.	2.9
Ni	0.2	0.0	0.8	0.35	0.06
Cu	2.4	0.3	0.7	2.2	0.05
Zn	14.	2.	0.0	22.	0.15
Se	0.13	0.02	0.007	0.05	0.1
Br	22.	0.5	8.2	0.0	0.08
Sr	0.06	0.2	0.5	0.3	0.009
Ba	1.4	0.6	0.0	14.	0.2
Pb	92.	2.2	17.	6.	9.2

to those calculated by Dzubay (11). There are no previous determinations of a fireworks component but the main ingredients of gunpowder are carbon, sulfur, and saltpeter (KNO_3) so a calculated potassium concentration of 44% seems reasonable. Tables 6 and 7 summarize the average predicted elemental concentrations along with the average observed concentrations for both months. The major elements, Al, Si, S, K, Ca, Fe, and Pb, are fit very closely. The overall fit for the remaining elements is also fairly good. However, the average point-by-point errors range up to a value of 348% for copper in the July data. Note, that despite the large point-by-point error, the average predicted and observed concentrations are very close, 8.3 and 9.0 ng/m^3, respectively. The disparity is due to the tendency of the target transformation rotation to produce profiles that represent the average composition of each source. Thus, even though the average fit for copper is very good, the point-by-point error indicates that this element has not been well represented. The problem is compounded by the large number of values below detection limits for many of the less abundant elements. The presence of source components that are too weak to be resolved can lead to distortions in the resolved element-profiles. For example, a paint-pigment factor was resolved in the August data but is apparently too weak to be resolved in the July data. It would be expected to be present in both months. The presence of an unresolved paint-pigment factor in the July data is manifested by the elevated titanium concentrations in the limestone and motor vehicle concentration profiles over those calculated for August. In addition, the very strong fireworks component could conceal the presence of any weaker factors.

The calculated mass concentration of the fireworks component for the six days around the Bicentennial Fourth of July celebration is plotted in Figure 2. A comparison of the predicted and total measured masses for all samples are given in Tables 8 and 9. The average deviations in the mass predictions are 16% for the July data and 12% for August. Table 10 summarizes the average mass contribution for each source to both the fine and coarse fractions. On the average during July and August, primary sulfate emissions accounted for about 60% of the mass in the fine fraction with motor vehicle emissions contributing 23% of the average July total and 21% in August. The two crustal components account for 95% of the coarse fraction in July and 84% in August.

DATA DIVIDED INTO PARTICLE-SIZE FRACTIONS

The data from RAPS station 112 were divided into fine and coarse subsets and the analysis repeated. To examine the effects caused by the presence of the fireworks factor, the fine-fraction data were analyzed both with and without the samples from July 4th and 5th. One sample, July 4th, noon to midnight, was excluded from the coarse fraction. Table 11 compares the average concentration of the elements in the fine fraction both with and without the July 4th samples. Removal of only 4 of the 99 samples resulted in significant changes in the average concentrations of four elements: Aluminum, potassium, strontium, and barium. These elements are the primary constituents of the fireworks factor.

Table 6. Summary of Mass Contributions. (ng/m^3)

RAPS Station 112, July 1976

Both Fractions

Element	Sulfate	Motor Vehicle	Soil	Limestone	Fireworks	Total Predicted	Total[a] Observed	Average[b] % Error
Al	17.	36.	1410.	0.0	29.	1500	1400 ± 200	18
Si	20.	10.	4460.	210.	4.	4710	4510 ± 660	45
S	1880.	11.	37.	8.	25.	1960	2020 ± 230	40
Cl	14.	3.4	30.	71.	7.0	125	130 ± 13	126
K	8.	0.0	300.	37.	233.	580	620 ± 143	27
Ca	0.0	8.	580.	660.	0.3	1240	1270 ± 160	19
Ti	9.4	8.9	32.	100.	0.0	150	170 ± 30	231
Mn	3.6	0.8	14.	6.9	0.7	26	27 ± 4	111
Fe	39.	22.	780.	110.	3.5	950	1020 ± 170	33
Ni	0.4	0.44	1.2	0.3	0.1	2.3	2.7 ± 0.4	89
Cu	2.4	2.1	0.2	2.6	1.0	8.3	9.0 ± 1.3	348
Zn	22.	4.8	0.0	17.	3.5	47	46 ± 5	199
Se	1.0	0.2	0.1	0.1	0.0	1.4	1.4 ± 0.2	131
Br	0.0	69.	10.	1.7	1.7	83	79 ± 7	34
Sr	0.0	0.0	3.3	1.0	4.8	9	10 ± 4	115
Ba	2.7	2.5	5.2	6.3	5.9	23	24 ± 4	104
Pb	57.	270.	25.	7.	1.1	360	360 ± 33	55

[a]Uncertainty is the standard deviation of the mean value.

[b]Average point-by-point error in predicted and measured data.

Table 7. Summary of Mass Contributions. (ng/m^3)

RAPS Station 112, August 1976

Both Fractions

Element	Motor Vehicle	Soil	Limestone	Paint	Sulfate	Total Predicted	Total[a] Observed	Average[b] % Error
Al	14.	580.	110.	12.	15.	730	710 ± 71	30
Si	0.0	2400.	55.	0.0	10.	2470	2440 ± 260	17
S	0.0	88.	0.0	0.0	2870.	2960	2810 ± 340	27
Cl	23.	39.	80.	7.	17.	160	170 ± 15	111
K	54.	200.	1.0	14.	12.	280	270 ± 18	34
Ca	0.0	610.	610.	12.	6.	1240	1250 ± 140	16
Ti	0.0	24.	23.	100.	14.	160	190 ± 37	255
Mn	8.9	13.	1.0	4.9	0.0	28	29 ± 4	90
Fe	16.	450.	110.	91.	37.	700	690 ± 66	14
Ni	0.8	0.0	1.6	0.2	0.7	3.4	3.2 ± 0.3	118
Cu	9.8	3.0	1.3	1.5	0.6	16	15 ± 2	147
Zn	56.	22.	0.0	15.	1.9	95	88 ± 8	102
Se	0.5	0.2	.001	.003	1.4	2.2	2.0 ± 0.2	65
Br	88.	5.	17.	0.0	1.	110	110 ± 8	28
Sr	0.2	2.1	1.1	0.2	0.1	3.7	3.7 ± 0.4	52
Ba	5.8	6.6	0.0	9.4	3.1	25	22 ± 5	331
Pb	370.	24.	34.	4.	120.	550	560 ± 54	1

[a]Uncertainty is the standard deviation of the mean value.

[b]Average point-by-point error in predicted and measured data.

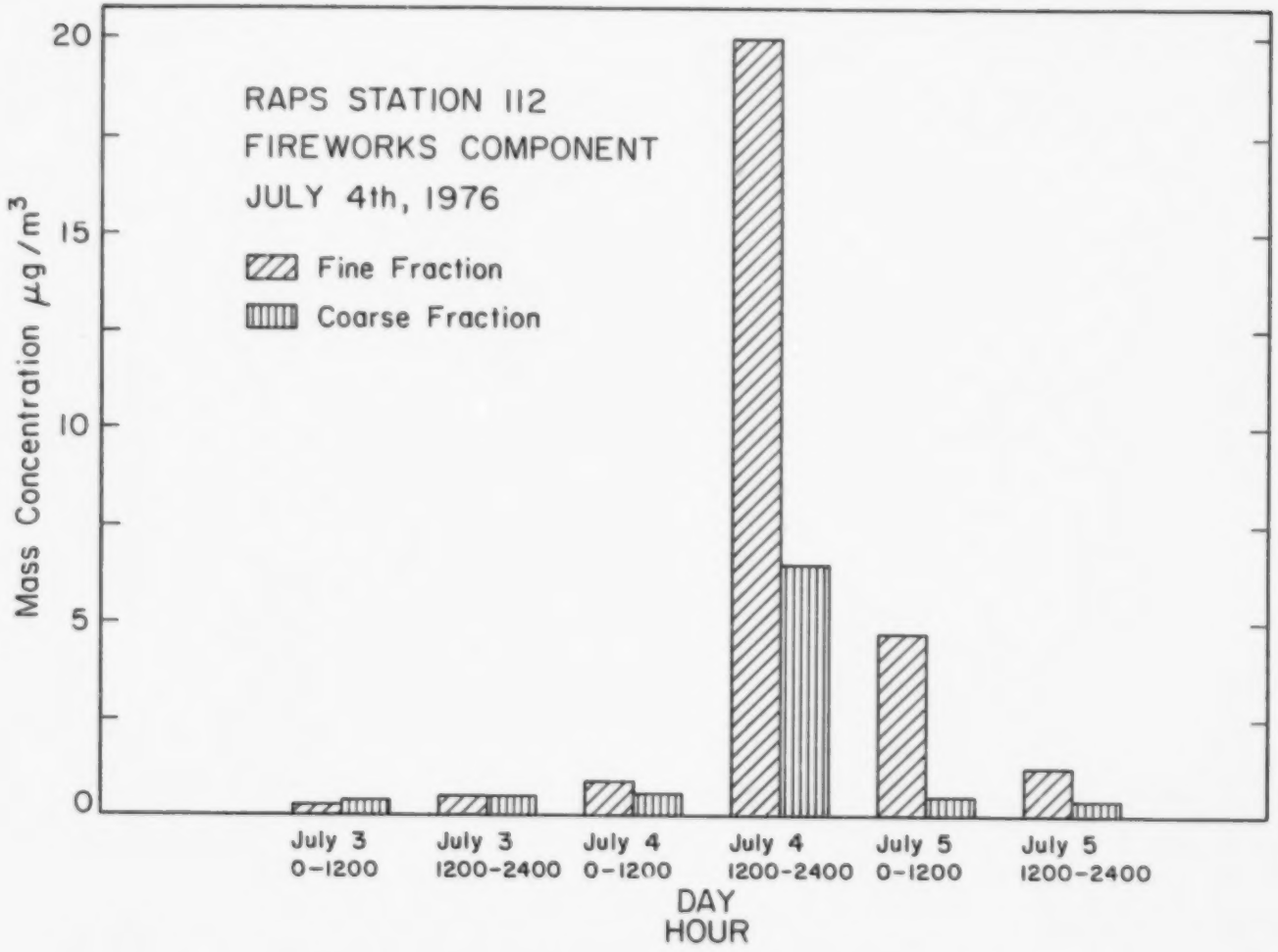

Figure 2. Mass concentration of the fireworks component for the six days around the Bicentennial Fourth of July Celebration. The maxiumum potassium concentration on July 4th was 13,000 ng/m^3.

Table 8. Predicted vs. Measured Sample Mass. ($\mu g/m^3$)

RAPS Station 112, July 1976

Both Fractions

Sample	Actual Mass	Calculated[a] Mass	% Deviation	Sample	Actual Mass	Calculated Mass	% Deviation
184-12f	26.0	23.5	-9.5	193- 0f	3.7	8.1	119.8
184-12c	19.8	21.0	6.1	193- 0c	17.7	22.6	27.9
185- 0f	34.1	32.0	-6.1	193-12f	10.5	10.5	-.5
185- 0c	16.2	15.3	-5.8	193-12c	16.4	23.2	41.6
185-12f	34.9	34.0	-2.6	194- 0f	9.2	10.3	12.2
185-12c	39.6	44.4	12.2	194- 0c	22.9	30.8	34.6
186- 0f	33.9	37.4	10.2	194-12f	21.3	17.1	-20.0
186- 0c	31.5	32.7	3.7	194-12c	23.1	33.0	42.9
186-12f	65.4	62.1	-5.0	195- 0f	17.2	17.5	1.6
186-12c	61.4	68.7	11.9	195- 0c	33.5	32.3	-3.5
187- 0f	*	24.2	-	195-12f	49.2	47.8	-2.9
187- 0c	28.1	30.1	7.2	195-12c	71.3	71.4	.2
187-12f	20.8	21.5	3.5	196- 0f	17.0	19.3	13.7
187-12c	14.8	20.7	39.9	196- 0c	44.5	52.1	17.1
188- 0f	32.8	34.5	5.0	196-12f	20.5	23.1	12.6
188- 0c	28.3	27.5	-3.0	196-12c	34.5	45.5	31.8
189-12f	*	19.5	-	197- 0f	15.5	15.5	.1
189-12c	*	195.2	-	197- 0c	32.1	41.1	28.0
190- 0f	26.8	21.1	-21.3	197-12f	10.4	9.6	-8.0
190- 0c	25.8	22.8	-11.5	197-12c	43.2	46.7	8.0
190-12f	35.8	33.8	-5.6	198- 0f	5.6	5.5	-1.3
190-12c	153.6	142.9	-7.0	198- 0c	12.3	15.2	23.9
191- 0f	32.2	23.6	-26.6	198-12f	6.3	8.5	35.0
191- 0c	36.4	46.2	26.8	198-12c	25.7	27.2	5.7
191-12f	28.8	23.0	-20.1	199- 0f	7.8	9.8	25.3
191-12c	37.3	45.4	21.7	199- 0c	39.1	32.0	-18.1
192- 0f	26.7	20.5	-23.2	199-12f	*	32.4	-
192- 0c	15.5	20.4	31.8	199-12c	189.7	161.4	-14.9
192-12f	5.9	9.3	57.9	200- 0f	*	38.8	-
192-12c	19.8	26.1	31.6	200- 0c	41.8	41.9	.3

*Missing value

Continued

[a]Experimental uncertainties are $\pm$ 3$\mu g/m^3$.

Sample coding: Day, time, and fraction, f=fine and c=coarse.

Table 8. Continued ($\mu g/m^3$)

RAPS Station 112, July 1976

Both Fractions

Sample	Actual Mass	Calculated Mass	% Deviation	Sample	Actual Mass	Calculated Mass	% Deviation
200-12f	28.8	36.0	25.0	206-12f	24.3	24.3	.1
200-12c	32.4	32.1	-.8	206-12c	38.4	32.9	-14.3
201- 0f	45.4	44.1	-2.8	207- 0c	*	23.0	-
201- 0c	48.8	48.2	-1.2	207-12f	34.5	32.7	-5.2
201-12f	40.2	39.2	-2.6	207-12c	46.9	53.5	14.1
201-12c	46.5	44.9	-3.5	208- 0f	33.6	28.5	-15.3
202- 0f	37.7	27.8	-26.3	208- 0c	28.1	32.3	15.1
202- 0c	51.6	54.4	5.5	208-12f	32.1	25.5	-20.4
202-12f	22.7	21.8	-4.1	208-12c	26.6	31.0	16.4
202-12c	65.7	70.6	7.5	209- 0f	21.7	17.3	-20.2
203- 0f	15.5	15.6	.7	209- 0c	11.9	13.1	10.3
203- 0c	38.4	40.2	4.7	209-12f	25.1	23.0	-8.4
204-12f	30.1	25.1	-16.5	209-12c	21.4	24.0	12.2
204-12c	36.8	49.9	35.6	210- 0f	22.7	16.8	-26.2
205- 0f	27.2	20.4	-25.1	210- 0c	21.4	25.7	20.0
205- 0c	31.3	37.2	18.8	210-12f	12.8	12.4	-3.4
205-12f	21.0	23.4	11.2	210-12c	14.1	16.2	15.0
205-12c	24.1	31.7	31.5	211- 0f	19.9	17.5	-12.3
206- 0f	13.1	10.7	-18.2	211- 0c	14.6	16.7	14.0
206- 0c	24.4	26.5	8.6	211-12f	49.8	41.7	-16.3
						Average Deviation =	15.7%[b]

[b]Average deviation is the sum of the absolute values of the error in the mass prediction for each sample divided by the number of samples.

Table 9. Predicted vs. Measured Sample Mass. ($\mu g/m^3$)

RAPS Station 112, August 1976

Both Fractions

Sample	Actual[a] Mass	Calculated Mass	% Deviation	Sample	Actual Mass	Calculated Mass	% Deviation
211-12c	35.2	38.8	10.2	220- 0c	8.4	7.3	-13.1
212- 0f	40.0	39.6	-1.1	220-12f	22.8	28.1	23.2
212- 0c	29.1	27.9	-4.2	220-12c	17.7	15.0	-15.1
212-12f	27.4	21.6	-21.4	221- 0f	23.6	28.2	19.5
212-12c	21.3	20.3	-4.7	221- 0c	12.8	11.4	-11.3
213- 0f	5.9	15.5	162.4	221-12f	28.7	30.5	6.1
213- 0c	7.9	9.7	22.7	221-12c	41.6	44.3	6.6
213-12f	28.4	21.4	-24.8	222- 0f	21.6	20.9	-3.3
213-12c	15.0	14.9	-.9	222- 0c	14.2	11.9	-16.5
214- 0f	7.8	8.4	7.8	222-12f	25.8	24.5	-5.1
214- 0c	6.7	6.5	-3.1	222-12c	25.3	23.5	-7.2
214-12f	9.0	8.9	-1.5	223- 0f	39.3	38.2	-2.8
214-12c	10.9	10.6	-2.7	223- 0c	33.6	33.4	-.7
215- 0f	17.1	18.9	10.3	223-12f	31.0	27.6	-11.0
215- 0c	18.5	16.8	-9.4	223-12c	23.7	20.8	-12.3
215-12f	18.8	17.9	-4.6	224- 0f	36.6	39.9	8.9
215-12c	18.5	16.5	-11.0	224- 0c	35.1	34.4	-2.0
216- 0f	22.8	24.3	6.6	224-12f	33.3	26.8	-19.7
216- 0c	38.0	42.7	12.2	224-12c	31.5	29.1	-7.7
216-12f	38.4	32.6	-15.2	225- 0f	33.0	29.8	-9.6
216-12c	30.5	28.5	-6.6	225- 0c	38.6	40.7	5.5
217- 0f	32.7	32.6	-.2	225-12f	32.8	27.2	-17.0
217- 0c	31.4	29.7	-5.5	225-12c	41.8	40.9	-2.2
217-12f	31.1	25.9	-16.6	226- 0f	39.6	28.9	-27.0
217-12c	24.3	23.9	-1.5	226- 0c	28.8	26.6	-7.5
218- 0f	30.2	27.8	-8.0	226-12f	44.1	30.8	-30.1
218- 0c	23.7	25.1	5.8	226-12c	29.4	28.9	-1.7
219-12f	19.5	19.0	-2.5	230- 0f	34.6	30.5	-12.0
219-12c	6.1	8.6	41.0	230- 0c	23.4	18.6	-20.6
220- 0f	16.4	14.0	-14.5	230-12f	43.8	41.0	-6.3

*Missing value

Continued

[a]Experimental uncertainties are $\pm$ 3$\mu g/m^3$.

Sample coding: Day, time, and fraction, f=fine and c=coarse.

Table 9. Continued ($\mu g/m^3$)

RAPS Station 112, August 1976

Both Fractions

Sample	Actual Mass	Calculated Mass	% Deviation	Sample	Actual Mass	Calculated Mass	% Deviation
230-12c	28.3	30.0	5.9	239-12c	35.5	36.5	2.8
231- 0f	44.3	42.6	-3.9	240- 0f	51.7	45.3	-12.5
231- 0c	28.2	27.4	-2.9	240- 0c	33.0	34.3	4.1
231-12f	62.9	59.7	-5.1	240-12c	33.7	35.3	4.6
231-12c	38.6	30.0	-22.4	241- 0f	24.6	20.5	-16.8
232- 0f	43.7	41.5	-5.1	241- 0c	*	22.1	-
232- 0c	28.2	26.8	-5.0	241-12f	11.1	13.4	20.4
232-12f	77.8	87.7	12.7	241-12c	26.6	28.9	8.7
232-12c	46.6	46.5	-.1	242- 0f	10.4	10.6	2.2
233- 0f	48.0	55.4	15.5	242- 0c	23.5	26.5	12.9
233- 0c	37.5	34.1	-9.1	242-12f	11.6	11.7	.5
237-12f	71.0	87.5	23.2	242-12c	16.2	20.3	25.6
237-12c	57.1	54.4	-4.8	243- 0f	21.4	15.7	-26.7
238- 0f	89.0	85.4	-4.1	243- 0c	18.7	22.3	19.3
238- 0c	60.1	60.3	.3	243-12f	33.6	37.4	11.3
238-12f	60.6	74.0	22.2	243-12c	*	53.4	-
238-12c	40.1	39.1	-2.6	244- 0f	33.6	31.6	-6.0
239- 0f	53.9	44.3	-17.8	244- 0c	45.1	48.0	6.3
239- 0c	32.6	28.2	-13.5	244-12f	34.2	15.1	-55.9
239-12f	44.7	34.7	-22.3	244-12c	*	41.7	-
						Average Deviation =	12.4%[b]

[b]Average deviation is the sum of the absolute values of the error in the mass prediction for each sample divided by the number of samples.

Table 10. Average mass contributions, both fine and coarse fractions. ($\mu g/m^3$)

RAPS Station 112

July 1976

Fraction	Sulfate	Motor Vehicle	Soil	Lime-stone	Fire-works	Total	Total Observed	% Deviation
Fine	14.8	5.8	2.1	0.3	0.9	23.9	25.2	5
Coarse	1.1	1.1	35.1	5.4	0.1	42.8	37.5	-14
Average	7.9	3.4	18.6	2.9	0.5	33.4	31.4	-6

August 1976

Fraction	Sulfate	Motor Vehicle	Soil	Lime-stone	Paint	Total	Total Observed	% Deviation
Fine	23.3	7.3	1.5	0.9	0.3	32.5	34.0	3
Coarse	2.5	0.9	20.2	3.9	1.0	28.2	28.2	4
Average	12.7	4.0	11.0	2.0	0.7	30.4	31.1	3

Table 11. Comparison of Data With and Without Samples From July 4th and 5th. (ng/m^3)

RAPS Station 112, July and August 1976

Fine Fraction

Element	With July 4th & 5th Mean	Without July 4th & 5th Mean[a]
Al	220 ± 30	200 ± 30
Si	440 ± 60	450 ± 60
S	4370 ± 310	4360 ± 320
Cl	90 ± 10	80 ± 9
K	320 ± 130	150 ± 9
Ca	110 ± 10	110 ± 10
Ti	63 ± 13	64 ± 13
Mn	17 ± 3	17 ± 3
Fe	220 ± 20	220 ± 20
Ni	2.3 ± 0.2	2.3 ± 0.2
Cu	16 ± 3	15 ± 3
Zn	78 ± 8	75 ± 8
Se	2.7 ± 0.2	2.7 ± 0.2
Br	140 ± 9	130 ± 8
Sr	5 ± 4	1.1 ± 0.1
Ba	19 ± 5	15 ± 4
Pb	730 ± 50	720 ± 50

[a]Mean value and standard deviation of the mean.

The results of the dimensionality tests for the fine and coarse fractions are given in Table 12. For the fine fraction without July 4th and 5th, there are large changes in the magnitude of the eigenvalues and chi square tests at both three and five retained factors. However, when the samples from those two days are included, the eigenvalue and Exner tests indicate four factors while the chi-square test indicates six. It appears that, in addition to fireworks, there are three major and two minor factors in the fine data. The two weaker factors, however, cannot be resolved when the samples from July 4th and 5th are included. For the coarse fraction the tests are inconclusive, indicating either four or five factors.

The target transformation analysis for the fine fraction without July 4th and 5th indicated the presence of a motor vehicle source, a sulfate source, a soil or flyash source, a paint-pigment source, and a refuse source. The presence of the sulfate, paint-pigment, and refuse factors was determined by the uniqueness test for the elements sulfur, titanium, and zinc respectively. In the paint-pigment factor, titanium was found to be associated with the elements sulfur, calcium, iron, and barium. The zinc factor, associated with the elements chlorine, potassium, iron, and lead, is attributed to refuse-incinerator emissions. This factor may also represent particles from zinc and/or lead smelters, though a high chlorine concentration is usually associated with particles from refuse incinerators (45). With July 4th and 5th included, the results indicated, in addition to the fireworks source, only the presence of motor vehicle, sulfate, and soil or flyash sources. Thus, we conclude that the presence of the fireworks factor inhibits the resolution of the weaker paint-pigment and refuse factors. The refined source profiles that best reproduced the fine data are listed in Table 13. The nature of the sulfate, motor vehicle, and paint-pigment source profiles are similar to those previously calculated for the July and August data. Except for the relative chlorine concentration, the calculated source profile for the refuse factor, with high concentrations of zinc and lead, is similar to that measured by Greenberg, et al. (45) for the Nicosia Municipal Incinerator near Chicago. The source profile of the soil factor is quite different than that calculated for the July and August data. The nature of this factor is more like that of coal flyash than soil, though the calculated sulfur concentration is higher than would be expected in flyash. Coal flyash emissions are expected to be found primarily in the fine fraction while crustal material, similar in composition, should be found in the coarse fraction. Thus, we conclude, that this factor is primarily the result of coal-burning power plant emissions. Neither the refuse nor flyash factors were resolved in the analyses of the data divided into July and August subsets. It seems additional factors are resolved when the data are divided into fine- and coarse-fraction subsets.

For the coarse fraction, the target transformation indicated the presence of two crustal factors, soil and limestone, a sulfate factor, and a paint-pigment factor. The refined source profiles that best reproduced the coarse fraction are listed in Table 14. The soil, limestone, and paint-pigment profiles are similar to those previously calculated for the August data. In addition, the paint-pigment source strongly resembles the factor calculated for the fine-fraction data. The only major difference is in the concentration of barium; unlike the fine fraction, the coarse-fraction

Table 12. Results of Dimensionality Tests

RAPS Station 112, July and August 1976

Fine Fraction July 4th and 5th Excluded

Factor	Eigenvalue	Chi Square	Exner	Average % Error
1	87.	210	.304	197
2	4.9	152	.304	197
3	2.0	57	.070	123
4	0.2	42	.050	98
5	0.1	26	.037	73
6	0.04	25	.029	69
7	0.02	26	.023	69
8	0.02	17	.019	67
9	0.01	16	.015	53

Fine Fraction, July 4th and 5th included

Factor	Eigenvalue	Chi Square	Exner	Average % Error
1	90.	210	.324	204
2	5.0	156	.214	164
3	1.7	65	.141	129
4	1.3	63	.064	93
5	0.16	55	.047	72
6	0.09	26	.034	68
7	0.03	24	.027	67
8	0.02	24	.021	58
9	0.02	16	.016	49

Coarse Fraction

Factor	Eigenvalue	Chi Square	Exner	Average % Error
1	96.	200	.216	73
2	2.4	70	.125	50
3	0.6	70	.089	45
4	0.29	59	.064	41
5	0.19	63	.040	35
6	0.07	61	.028	33
7	0.03	38	.019	28
8	0.02	26	.013	23
9	0.01	30	.009	22

Table 13. Refined Source Profiles. (mg/g)

RAPS Station 112, July and August 1976

Fine Fraction Without July 4th and 5th

Element	Motor Vehicle	Sulfate	Flyash/ Soil	Paint	Refuse
Al	5.	1.1	53.	0.0	0.0
Si	0.0	1.9	130.	0.0	7.
S	0.2	240.	19.	6.	0.0
Cl	2.4	1.1	0.0	4.6	22.
K	1.4	1.6	15.	5.7	48.
Ca	11.	0.0	16.	34.	1.2
Ti	0.0	0.7	2.5	110.	0.0
Mn	0.0	0.0	0.7	4.8	8.6
Fe	0.0	1.1	36.	90.	36.
Ni	0.08	0.04	0.042	0.011	0.7
Cu	0.6	0.01	0.0	0.0	8.7
Zn	0.8	0.0	0.0	3.7	65.
Se	0.1	0.1	0.001	0.2	0.2
Br	30.	0.3	2.5	0.0	0.05
Sr	0.09	0.01	0.15	0.1	0.001
Ba	0.7	0.035	0.07	28.	0.5
Pb	107.	6.5	5.	0.0	46.

Fine Fraction, Including July 4th and 5th

Element	Motor Vehicle	Sulfate	Flyash/ Soil	Fireworks
Al	3.	0.9	62.	60.
Si	0.0	2.8	140.	0.0
S	0.0	232.	14.	26.
Cl	5.2	1.6	0.31	19.
K	0.0	0.06	43.	580.
Ca	12.	0.006	17.	0.27
Ti	2.8	1.8	2.3	0.0
Mn	1.5	0.1	0.8	3.6
Fe	5.8	3.8	38.	9.
Ni	0.2	0.06	0.05	0.3
Cu	1.9	0.2	0.03	4.6
Zn	9.8	1.4	0.0	24.
Se	0.1	0.1	0.0	0.01
Br	26.	0.0	2.7	2.
Sr	0.0	0.0	0.9	12.
Ba	1.45	0.3	0.8	15.
Pb	105.	8.	3.8	0.0

Table 14. Refined Source Profiles. (mg/g)

RAPS Station 112, July and August 1976

Coarse Fraction

Element	Soil	Limestone	Sulfate	Paint
Al	71.	30.	28.	5.
Si	274.	150.	0.0	0.0
S	4.9	0.0	90.	37.
Cl	1.4	16.	3.6	6.9
K	19.	15.	9.3	0.0
Ca	40.	188.	0.08	25.
Ti	0.0	1.5	0.0	128.
Mn	0.8	1.6	1.	1.2
Fe	40.	34.	43.	65.
Ni	0.01	0.2	0.2	0.06
Cu	0.0	0.6	0.9	0.0
Zn	0.0	4.2	4.3	0.3
Se	0.01	0.02	0.13	0.001
Br	0.5	3.1	3.8	1.3
Sr	0.2	0.3	0.2	0.1
Ba	0.6	0.7	0.4	3.2
Pb	1.5	11.	13.	6.7

profile does not associate barium with the paint-pigment factor. The calculated sulfur concentration in the coarse-fraction sulfate factor is much less than that in the fine fraction and there are sizable concentrations of elements such as aluminum, iron, and lead not found in the fine-fraction profile. The origin of this factor is not clear. One possible explanation is that a small part of the sulfate particles in the fine fraction ended up in the coarse samples, though a correction for this possibility was made by Goulding, et al. (31) in the original analyses of the samples. Another possible explanation is the transformation of gaseous sulfur dioxide into sulfates on the surface of the coarse particles. Carbon soot and iron- or manganese-containing particles can catalyze the conversion of SO_2 to sulfates that would adhere to the particles in the coarse fraction. Tables 15 and 16 summarize the average elemental concentrations along with the average observed concentrations for the fine fraction. Again, the fit for the major elements is fairly good. With the addition of the two extra factors to the data without July 4th and 5th, a much better fit for the concentrations of zinc and titanium was obtained. Table 17 summarizes the mass contributions for the coarse fraction. Here, all the elements are fit reasonably well. A comparison of the predicted and measured sample masses are listed in Tables 18 and 19. The average deviations in the mass predictions are 16% for the fine data and 12% for the coarse. Figure 3 summarizes the average mass contribution for each source to the total measured sample mass. The low percentage of unaccounted sample mass is expected in this type of analysis since the regression fit calculates scaling factors so as to minimize the difference between the measured and predicted sample mass. The predicted motor vehicle concentration of only 15% is less than that calculated for the same data divided by months. However, in the previous calculations, the measured lead concentration was accounted for exclusively by the motor vehicle factor. With the addition of the refuse factor, the measured lead concentration is now divided among the two factors. Here, the lead contribution is 70% from motor vehicle emissions and 10% from refuse incinerators. Dzubay (11) estimated that motor vehicle emissions contributed 8% of the fine-fraction mass in St. Louis. In the coarse fraction, the two crustal components account for 80% of the total mass.

Though carbon was not among the elements analyzed by Goulding, et al. (31), it is possible to estimate the carbon concentration resulting from each of the resolved sources. Watson (12) and Pierson (46) measured carbon concentrations in particles from motor vehicle emissions of around 500 mg/g. If this concentration were used in the present study, it would result in an average carbon contribution from motor vehicles of around 2,500 ng/m^3, or about nine percent of the average fine-fraction mass. Additional amounts of carbon may be associated with the sulfate and refuse factors. Flyash would contribute a negligible amount of carbon (47). For the coarse fraction, Mason (37) reports carbon concentrations in shale and limestone of 2% and 11% respectively. Thus, the two crustal factors would represent a carbon concentration of about 2000 ng/m^3. If the sulfate factor in the coarse fraction indeed represents the catalyzation of SO_2 to SO_4 by carbon soot, then it would provide an additional source of carbonaceous particles.

Table 15. Summary of Mass Contributions. (ng/m^3)

RAPS Station 112, July and August 1976

Samples From July 4th and 5th Excluded

Element	Fine Fraction: Motor Vehicle	Sulfate	Flyash/ Soil	Paint	Refuse	Total Predicted	Total[a] Observed	Average[b] % Error
Al	23.	21.	170.	0.0	0.0	220	200 ± 24	29
Si	0.1	36.	420.	0.0	9.	470	450 ± 59	15
S	0.1	4570.	62.	2.5	0.0	4630	4360 ± 320	7
Cl	11.	21.	0.0	2.0	27.	61	80 ± 9	163
K	6.	30.	49.	2.3	60.	150	150 ± 9	28
Ca	50.	0.0	52.	14.	1.5	120	110 ± 10	53
Ti	0.0	12.	8.	45.	0.0	66	64 ± 13	260
Mn	0.0	0.0	2.3	2.0	11.	15	17 ± 3	121
Fe	0.0	21.	120.	37.	45.	220	220 ± 19	15
Ni	0.4	0.8	0.1	0.0	0.9	2.1	2.2 ± 0.2	106
Cu	2.7	0.2	0.0	0.0	11.	14	15 ± 2	212
Zn	3.6	0.0	0.0	1.5	81.	86	75 ± 8	78
Se	0.4	2.1	0.0	0.1	0.2	2.8	2.7 ± 0.2	89
Br	135.	4.5	8.2	0.0	0.0	144	132 ± 8	27
Sr	0.4	0.2	0.5	0.0	0.0	1.2	1.1 ± 0.1	88
Ba	3.2	0.9	0.2	11.	0.6	16	15 ± 4	353
Pb	480.	120.	16.	0.0	57.	680	720 ± 53	6

[a]Uncertainty is the standard deviation of the mean value.

[b]Average point-by-point error in predicted and measured data.

Table 16. Summary of Mass Contributions. (ng/m^3)

RAPS Station 112, July and August 1976

Including Samples From July 4th and 5th

Fine Fraction

Element	Motor Vehicle	Sulfate	Flyash/ Soil	Fireworks	Total Predicted	Total[a] Observed	Average[b] % Error
Al	16.	17.	176.	20.	230	220 ± 31	29
Si	0.0	54.	398.	0.0	450	440 ± 57	12
S	0.0	4495.	40.	8.5	4540	4370 ± 310	5
Cl	28.	31.	0.9	6.2	66	85 ± 9	194
K	0.0	1.2	122.	190.	310	320 ± 130	11
Ca	64.	0.1	48.	0.1	112	112 ± 10	72
Ti	15.	35.	6.5	0.0	56	63 ± 13	655
Mn	8.0	2.7	2.2	1.2	14	17 ± 3	175
Fe	31.	74.	108.	3.0	215	217 ± 19	49
Ni	1.0	1.1	0.1	0.1	2.3	2.3 ± 0.2	128
Cu	10.	3.5	0.1	1.5	15	16 ± 2	261
Zn	52.	27.	0.0	7.9	87	78 ± 8	131
Se	0.6	2.1	0.0	0.0	2.8	2.7 ± 0.2	89
Br	138.	0.0	7.7	0.7	146	137 ± 9	31
Sr	0.0	0.0	2.5	3.8	6.3	5.3 ± 4.0	294
Ba	7.7	5.8	2.3	4.9	21	19 ± 5	303
Pb	557.	155.	11.	0.0	723	725 ± 51	2

[a]Uncertainty is the standard deviation of the mean value.

[b]Average point-by-point error in predicted and measured data.

Table 17. Summary of Mass Contributions. (ng/m^3)

RAPS Station 112, July and August 1976

Coarse Fraction

Element	Soil	Limestone	Sulfate	Paint	Total Predicted	Total[a] Observed	Average[b] % Error
Al	1365.	272.	111.	125.	1760	1840 ± 180	12
Si	5266.	1359.	0.0	0.0	6630	6400 ± 580	4
S	94.	0.0	356.	92.	543	490 ± 32	35
Cl	27.	145.	14.	17.	200	210 ± 213	72
K	365.	136.	37.	0.0	540	540 ± 50	9
Ca	769.	1703.	0.3	62.	2540	2380 ± 141	8
Ti	0.0	14.	0.0	320.	330	300 ± 43	107
Mn	15.	15.	4.0	3.0	37	39 ± 4	37
Fe	769.	308.	168.	162.	1410	1470 ± 158	11
Ni	0.2	2.0	0.8	0.1	3.2	3.6 ± 0.4	155
Cu	0.0	5.8	3.6	0.0	9.4	8.9 ± 0.8	149
Zn	0.0	38.	17.	0.7	56	56 ± 6	126
Se	0.2	0.2	0.5	0.0	0.9	0.7 ± 0.04	154
Br	8.8	28.	15.	3.2	55	51 ± 3	51
Sr	3.8	2.4	0.7	0.3	7.2	7.9 ± 0.8	21
Ba	11.	6.3	1.4	8.0	27	27 ± 3	53
Pb	29.	100.	52.	17.	197	193 ± 11	47

[a]Uncertainty is the standard deviation of the mean value.

[b]Average point-by-point error in predicted and measured data.

Table 18. Predicted vs Measured sample mass ($\mu g/m^3$)

RAPS Station 112, July and August 1976

Fine Fraction

Sample	Actual[a] Mass	Calculated Mass	% Deviation	Sample	Actual Mass	Calculated Mass	% Deviation
184-12f	26.0	23.4	-9.9	202-12f	22.7	27.8	22.6
185- 0f	34.1	33.6	-1.6	203- 0f	15.5	18.4	19.0
185-12f	34.9	33.0	-5.6	204-12f	30.1	31.4	4.4
188- 0f	32.8	36.1	10.2	205- 0f	27.2	24.4	-10.4
189-12f	*	20.6	-	205-12f	21.0	22.1	5.4
190- 0f	26.8	21.1	-21.1	206- 0f	13.1	10.8	-17.9
190-12f	35.4	34.5	-2.7	206-12f	24.3	24.8	2.1
191- 0f	32.2	23.6	-26.8	207-12f	34.5	33.6	-2.7
191-12f	28.8	23.2	-19.6	208- 0f	33.6	29.5	-12.3
192- 0f	26.7	20.9	-21.8	208-12f	32.1	26.2	-18.4
192-12f	5.9	8.9	51.4	209- 0f	21.7	17.2	-20.9
193- 0f	3.7	8.3	124.5	209-12f	25.1	23.9	-4.6
193-12f	10.5	10.8	2.8	210- 0f	22.7	17.3	-23.7
194- 0f	9.2	11.2	22.2	210-12f	12.8	11.4	-10.6
194-12f	21.3	16.5	-22.7	211- 0f	19.9	16.0	-19.4
195- 0f	17.2	19.3	12.3	211-12f	49.8	43.1	-13.5
195-12f	49.2	51.1	3.8	212- 0f	40.2	38.8	-3.6
196- 0f	17.0	22.3	31.1	212-12f	27.4	21.4	-21.9
196-12f	20.5	26.1	27.2	213- 0f	5.9	15.2	157.5
197- 0f	15.5	17.3	11.4	213-12f	28.4	21.3	-25.2
197-12f	10.4	10.2	-1.9	214- 0f	7.8	8.4	8.2
198- 0f	5.6	5.8	3.1	214-12f	9.0	8.9	-1.3
198-12f	6.3	7.4	18.2	215- 0f	17.1	19.4	13.2
199- 0f	7.8	8.7	11.6	215-12f	18.8	18.0	-4.3
199-12f	*	34.2	-	216- 0f	22.8	26.2	15.0
200- 0f	*	35.9	-	216-12f	38.4	32.9	-14.2
200-12f	28.8	37.2	29.2	217- 0f	32.7	31.8	-2.9
201- 0f	45.4	45.2	-.5	217-12f	31.1	26.3	-15.5
201-12f	40.2	40.2	-.1	218- 0f	30.2	27.9	-7.7
202- 0f	37.7	30.0	-20.3	219-12f	19.5	19.0	-2.5

*Missing value

Continued

[a]Experimental uncertainties are $\pm$ 3$\mu g/m^3$.

Sample coding: Day, time, and fraction, f=fine and c=coarse.

Table 18. Continued ($\mu g/m^3$)

RAPS Station 112, July and August 1976

Fine Fraction

Sample	Actual Mass	Calculated Mass	% Deviation	Sample	Actual Mass	Calculated Mass	% Deviation
220- 0f	16.4	14.1	-13.8	232- 0f	43.7	41.7	-4.7
220-12f	22.8	27.5	20.4	232-12f	77.8	86.5	11.2
221- 0f	23.6	27.9	18.3	233- 0f	48.0	55.2	15.1
221-12f	28.7	30.1	4.9	237-12f	71.0	86.6	22.0
222- 0f	21.6	20.4	-5.5	238- 0f	89.0	84.8	-4.8
222-12f	25.8	25.5	-1.3	238-12f	60.6	74.2	22.4
223- 0f	39.3	39.7	.9	239- 0f	53.9	44.1	-18.1
223-12f	31.0	27.8	-10.5	239-12f	44.7	35.2	-21.3
224- 0f	36.6	40.1	9.5	240- 0f	51.7	45.2	-12.5
224-12f	33.3	27.2	-18.4	241- 0f	24.6	20.6	-16.3
225- 0f	33.0	30.8	-6.8	241-12f	11.1	12.3	11.1
225-12f	32.8	27.1	-17.3	242- 0f	10.4	10.2	-2.3
226- 0f	39.6	28.6	-27.9	242-12f	11.6	11.2	-3.4
226-12f	44.1	31.0	-29.6	243- 0f	21.4	16.3	-23.7
230- 0f	34.6	29.6	-14.3	243-12f	33.6	38.9	15.9
230-12f	43.8	40.8	-6.9	244- 0f	33.6	31.9	-4.9
231- 0f	44.3	42.4	-4.3	244-12f	34.2	16.3	-52.3
231-12f	62.9	59.7	-5.1				

Average Deviation = 16.2%[b]

[b]Average deviation is the sum of the absolute values of the error in the mass prediction for each sample divided by the number of samples.

Table 19. Predicted vs. Measured Sample Mass ($\mu g/m^3$).

RAPS Station 112, July and August 1976

Coarse Fraction

Sample	Actual Mass	Calculated[a] Mass	% Deviation	Sample	Actual Mass	Calculated Mass	% Deviation
184-12c	19.8	19.9	.6	201- 0c	48.8	46.6	-4.6
185- 0c	16.2	18.9	16.8	201-12c	46.5	42.4	-8.9
185-12c	39.6	45.2	14.0	202- 0c	51.6	51.1	-.9
186- 0c	31.5	32.4	2.9	202-12c	65.7	67.2	2.2
187- 0c	28.1	29.1	3.6	203- 0c	38.4	39.9	3.9
187-12c	14.8	19.1	28.9	204-12c	36.8	47.3	28.6
188- 0c	28.3	26.4	-6.9	205- 0c	31.3	36.9	17.7
189-12c	*	205.3	-	205-12c	24.1	28.7	19.0
190- 0c	25.8	21.1	-18.2	206- 0c	24.4	24.0	-1.7
190-12c	153.6	147.0	-4.3	206-12c	38.4	30.6	-20.3
191- 0c	36.4	44.0	21.0	207- 0c	*	23.5	-
191-12c	37.3	42.0	12.5	207-12c	46.9	45.4	-3.3
192- 0c	15.5	18.6	20.0	208- 0c	28.1	31.8	13.1
192-12c	19.8	23.2	17.1	208-12c	26.6	28.3	6.4
193- 0c	17.7	20.5	15.6	209- 0c	11.9	12.5	5.0
193-12c	16.4	22.0	34.3	209-12c	21.4	26.5	23.9
194- 0c	22.9	29.3	27.8	210- 0c	21.4	25.3	18.4
194-12c	23.1	30.4	31.6	210-12c	14.1	14.7	4.0
195- 0c	33.5	31.4	-6.2	211- 0c	14.6	15.9	9.2
195-12c	71.3	71.9	.8	211-12c	35.2	40.3	14.6
196- 0c	44.5	50.2	12.8	212- 0c	29.1	29.9	2.9
196-12c	34.5	43.2	25.3	212-12c	21.3	20.2	-5.1
197- 0c	32.1	40.0	24.7	213- 0c	7.9	9.2	15.9
197-12c	43.2	45.3	4.8	213-12c	15.0	14.9	-.7
198- 0c	12.3	14.3	15.9	214- 0c	6.7	6.6	-2.2
198-12c	25.7	23.6	-8.1	214-12c	10.9	9.9	-9.5
199- 0c	39.1	32.2	-17.6	215- 0c	18.5	17.1	-7.6
199-12c	189.7	168.5	-11.2	215-12c	18.5	15.7	-15.0
200- 0c	41.8	44.6	6.6	216- 0c	38.0	45.3	19.2
200-12c	32.4	31.4	-3.2	216-12c	30.5	27.5	-9.7

*Missing value

Continued

[a]Experimental uncertainties are $\pm$ 3$\mu g/m^3$.

Sample coding: Day, time, and fraction, f=fine and c=coarse.

Table 19. Continued ($\mu g/m^3$)

RAPS Station 112, July and August 1976

Coarse Fraction

Sample	Actual Mass	Calculated Mass	% Deviation	Sample	Actual Mass	Calculated Mass	% Deviation
217- 0c	31.4	29.4	-6.3	231- 0c	28.2	26.9	-4.7
217-12c	24.3	23.8	-2.2	231-12c	38.6	29.9	-22.7
218- 0c	23.7	23.7	.1	232- 0c	28.2	26.6	-5.8
219-12c	6.1	9.9	62.5	232-12c	46.6	44.7	-4.1
220- 0c	8.4	8.4	.3	233- 0c	37.5	32.8	-12.6
220-12c	17.7	14.1	-20.2	237-12c	57.1	53.7	-5.9
221- 0c	12.8	11.7	-8.8	238- 0c	60.1	63.1	5.1
221-12c	41.6	42.8	2.8	238-12c	40.1	39.8	-.7
222- 0c	14.2	11.8	-17.2	239- 0c	32.6	29.3	-10.3
222-12c	25.3	25.1	-.9	239-12c	35.5	36.2	2.0
223- 0c	33.6	36.7	9.2	240- 0c	33.0	32.6	-1.2
223-12c	23.7	20.5	-13.6	240-12c	24.6	34.7	41.2
224- 0c	35.1	33.3	-5.3	241- 0c	*	20.9	-
224-12c	31.5	28.1	-10.9	241-12c	26.6	26.2	-1.4
225- 0c	38.6	38.8	.6	242- 0c	23.5	25.1	6.6
225-12c	41.8	39.1	-6.4	242-12c	16.2	18.6	14.5
226- 0c	38.8	25.4	-34.5	243- 0c	18.7	22.5	20.1
226-12c	29.4	28.5	-3.1	243-12c	*	54.4	-
230- 0c	23.4	18.2	-22.4	244- 0c	45.1	51.3	13.8
230-12c	28.3	29.8	5.3	244-12c	*	39.6	-
					Average Deviation =		11.7%[b]

[b]Average deviation is the sum of the absolute values of the error in the mass prediction for each sample divided by the number of samples.

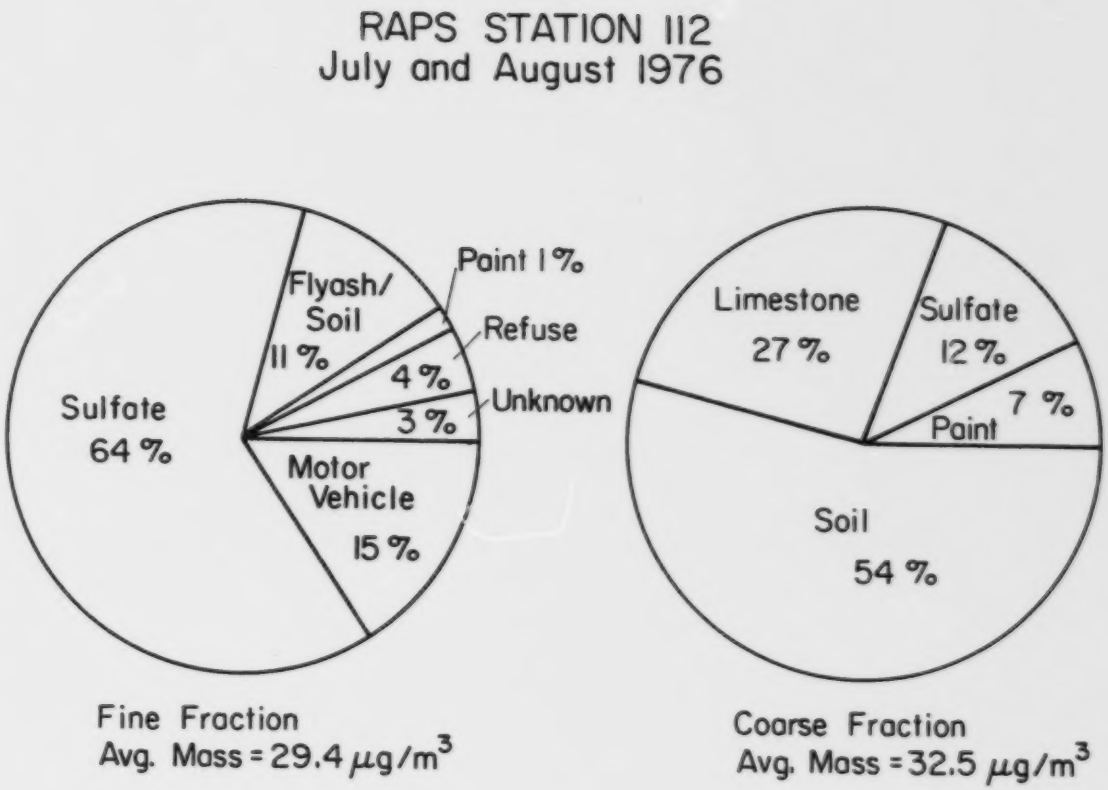

Figure 3. Average mass contribution of each source to the fine- and coarse-fraction samples from RAPS station 112 during July and August 1976.

SECTION 8

RESULTS FOR ONE WEEK AT ALL RAPS STATIONS

DATA DIVIDED BY DAYS

The data from all RAPS stations for one week were first divided into groups corresponding to the days Saturday, Sunday, and Monday (SSM) and to the days Tuesday, Wednesday, Thursday, and Friday (TWTF). Each group was analyzed separately. The results of the dimensionality tests are given in Table 20. For the SSM data, the tests seem to indicate that five factors are needed to represent the data. The test results for TWTF give no real indication of the correct number of factors.

The target transformation analysis for the SSM data indicated the presence of two crustal factors, a motor vehicle factor, a sulfur factor, and a steel factor. The sulfate and steel factors were derived from the uniqueness test. The results for TWTF were similar to those for SSM. However, as more factors were retained, additional elements were found to be unique. With six retained factors aluminum was unique, titanium at seven, and zinc at eight. As a result, four separate sets of test vectors were analyzed. Sulfate, motor vehicle, soil, limestone, and steel with five factors, and the addition of aluminum with six factors, titanium with seven, and zinc with eight.

The scaled source profiles that best reproduced the SSM data are given in Table 21. The motor vehicle factor has a lead concentration of 16% and a bromine to lead ratio of 0.14. This factor also has a calculated zinc concentration of 7%. The low bromine to lead ratio and the high zinc concentration indicate a combination of two factors, one arising from motor vehicle exhaust and the other from lead and/or zinc smelters. Attempts to resolve the SSM lead factor into two distinct sources were unsuccessful. The concentration of silicon in the soil factor and calcium in the limestone are somewhat lower than those calculated for RAPS station 112. These results indicate the presence of a number of weaker, unresolved sources that are diluting the elemental concentrations of the calculated source profiles. The iron concentration in the steel factor of 42% is much less than the 57% used by Dzubay (11) in his study of the RAPS data.

For the TWTF data, reasonable fits could be made with either five, six, seven, or eight factors. However, the scaling factors calculated by the regression analysis in all four cases produced physically impossible results,

Table 20. Results of Dimensionality Tests.

One Week, All RAPS Stations

SSM

Factor	Eigenvalue	Chi Square	Exner	Average % Error
1	67.5	810	.7474	290
2	47.8	120	.2337	108
3	1.7	130	.1916	104
4	1.1	207	.1573	72
5	1.0	45	.1202	63
6	.5	44	.0938	66
7	.3	58	.0766	59
8	.3	43	.0310	40
9	.2	35	.0161	28

TWTF

Factor	Eigenvalue	Chi Square	Exner	Average % Error
1	90.0	920	.7302	373
2	61.1	140	.2163	134
3	2.2	130	.1710	135
4	1.5	98	.1314	127
5	.9	70	.1023	122
6	.6	45	.0669	127
7	.2	48	.0528	140
8	.2	37	.0376	45
9	.1	29	.0260	40

Table 21. Refined Source Profiles (mg/g).

One Week, All RAPS Stations

SSM

Element	Motor Vehicle	Soil	Limestone	Sulfate	Steel
Al	15.	163.	1.6	0.43	68.
Si	0.0	239.	129.	1.	0.0
S	1.	3.2	12.9	184.	0.0
Cl	21.	5.4	12.	0.0	72.
K	16.	25.	14.	5.4	11.
Ca	13.	4.9	152.	4.	18.
Ti	7.8	15.	0.0	0.0	25.
Mn	0.4	0.0	0.45	0.57	13.
Fe	0.0	36.	18.	7.	416.
Cu	7.9	0.72	0.07	0.33	2.6
Zn	69.	0.0	3.2	0.0	17.
Se	0.78	0.17	0.0	0.08	0.06
Br	23.	1.50	0.87	1.60	4.60
Ba	3.1	2.2	0.31	0.21	2.3
Pb	160.	1.5	5.1	4.5	0.0

i.e. negative scaling factors or scaling factors that resulted in concentrations of over one hundred percent. These results would seem to indicate that the TWTF data are probably composed of sources that are significantly different at each station. A source resolution by factor analysis is impossible when the number of sources approaches the number of elements in the analysis. The fifteen elements retained in the TWTF data may well be insufficient to permit a resolution of all the sources that are significant at each station. With such a limited number of elements, only the major sources are resolved. Perhaps, if data for more elements were available, it would be possible to produce a more sensitive resolution of sources. In an attempt to reduce the number of possible sources, the TWTF data were further subdivided. The subsets were composed of the samples collected at all stations on days Tuesday and Wednesday and on days Thursday and Friday. The results were the same. We must conclude that large differences in the nature of the source contributions at each station will preclude an analysis of a data set composed of samples from all stations. Table 22 summarizes the elemental concentrations along with the observed concentrations for the SSM data. Figure 4 plots the average mass concentration for the five sources at each station. The steel factor contributes significantly to the total mass only in the coarse fraction at stations 103, 105, 106, and 108. These stations are located in the heavily industrialized sections of the sampling area and in close proximity to the iron works and foundries. A comparison of the predicted and total measured sample masses are given in Table 23. The average deviation between predicted and measured masses is significantly poorer than those previously calculated for station 112. These larger errors are attributed to the presence of different sources at each station that cannot be accounted for by the average concentration profiles produced by this analysis. Table 24 summarizes the average mass contribution for each source for both fine and coarse fractions. On the average, the sulfate aerosol accounts for over 80% of the mass in the fine fraction with motor vehicle emissions contributing an additional 11%. In the coarse fraction, the two crustal components account for about 84% of the total mass.

DATA DIVIDED INTO PARTICLE-SIZE FRACTIONS

The analysis of the data from all RAPS stations for one week was repeated with the data divided into fine- and coarse-particle subsets. The results of the dimensionality tests for both fractions are given in Table 25. In both cases there are no clear indicators of the correct number of factors to be retained. The tests for the fine fraction seem to indicate either four or five factors and for the coarse fraction, five or six.

The target transformation analysis of the fine fraction produced identical results for both four and five factors, indicating that four should be a sufficient number of factors to represent the data. The factors determined by the target transformation analysis were motor vehicle, sulfate, smelters, and steel. The smelter factor was determined by the uniqueness test for the element zinc and was found to be associated with lead. Gatz (16), noted the presence of a zinc/lead factor and attributed it to smelters located primarily in the East St. Louis and Granite City areas. A smelter factor was not resolved in the

Table 22. Summary of Mass Contributions. (ng/m^3)

One Week, All RAPS Stations

SSM

Element	Motor Vehicle	Soil	Limestone	Sulfate	Steel	Total Predicted	Total[a] Observed	Average[b] % Error
Al	16.	270.	4.4	3.0	32.	330	320 ± 30	35
Si	0.0	400.	354.	6.9	0.0	760	760 ± 80	21
S	1.0	5.4	35.	1270.	0.0	1320	1310 ± 130	5
Cl	22.	9.0	34.	0.0	34.	99	98 ± 12	275
K	16.	43.	38.	37.	5.1	139	134 ± 9	46
Ca	13.	8.3	420.	29.	8.4	470	470 ± 50	97
Ti	7.9	25.	0.0	0.0	12.	45	45 ± 9	189
Mn	0.40	0.0	1.2	4.0	60.	12	12 ± 1	94
Fe	0.0	60.	48.	49.	200.	360	360 ± 42	9
Cu	8.0	1.2	0.2	2.3	1.2	13	13 ± 2	182
Zn	70.	0.0	8.7	0.0	8.0	87	93 ± 20	120
Se	0.8	0.3	0.0	0.5	0.03	1.6	1.6 ± 0.2	106
Br	23.	2.5	2.4	11.	2.2	41	37 ± 3	57
Ba	3.1	3.7	0.9	1.5	1.1	10	9 ± 1	142
Pb	160.	2.5	14.	31.	0.0	210	210 ± 20	61

[a]Uncertainty is the standard deviation of the mean value.

[b]Average point-by-point error in predicted and measured data.

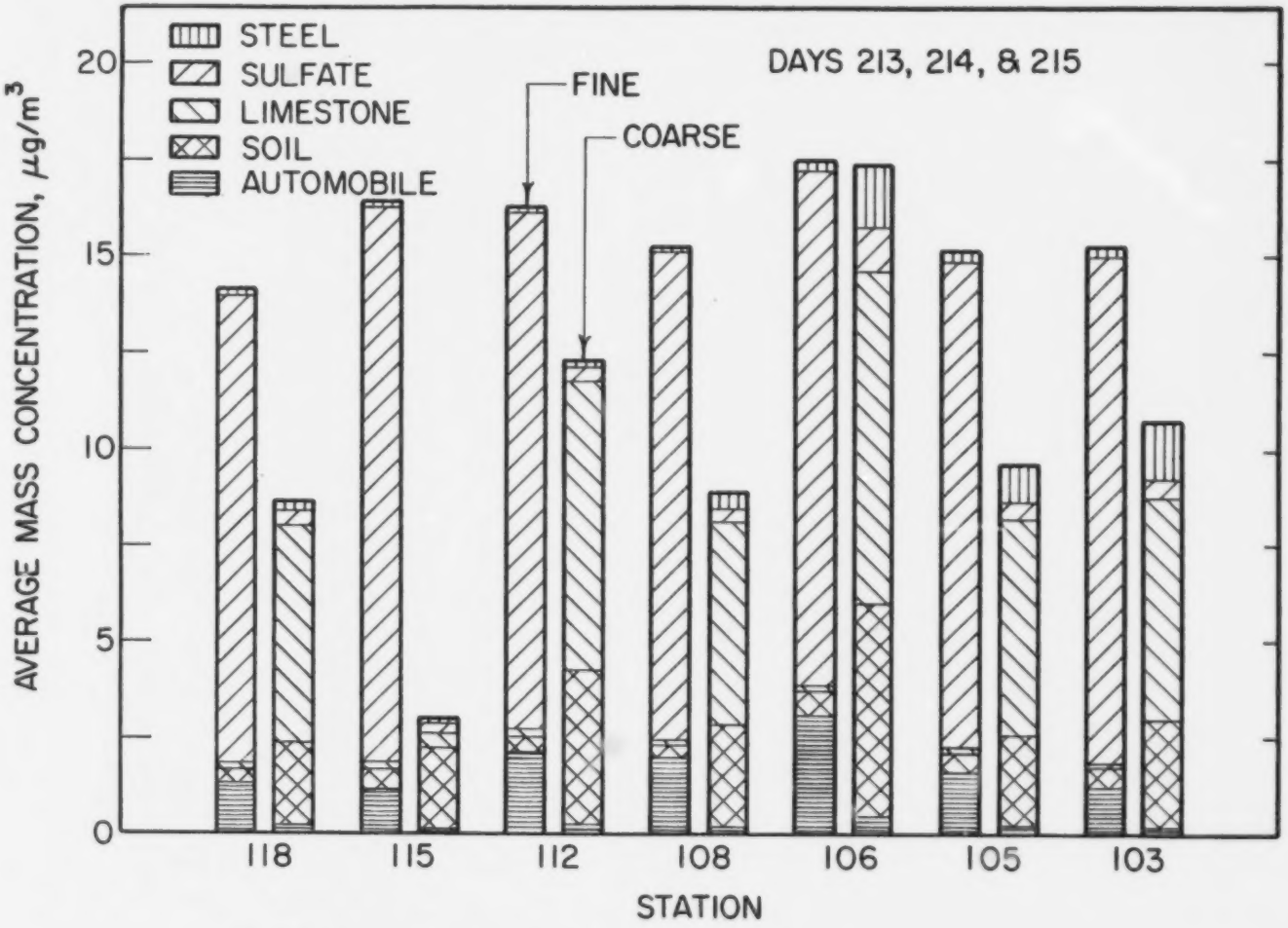

Figure 4. A comparison of the calculated mass concentrations of the five source components at all RAPS stations. Both fine and coarse fractions are plotted at each station. These samples are from days Saturday, Sunday, and Monday.

Table 23. Predicted vs. Measured Sample Mass ($\mu g/m^3$).

One Week, All RAPS Stations

SSM

Sample	Actual Mass	Calculated[a] Mass	% Deviation	Sample	Actual Mass	Calculated Mass	% Deviation
05-13- 0-1	11.0	16.8	52.3	03-13-12-1	26.9	26.6	-1.0
05-13- 0-2	6.9	8.1	17.9	03-13-12-2	13.7	11.4	-16.7
05-13- 6-1	15.8	15.9	.4	03-13-18-1	27.2	26.4	-3.1
05-13- 6-2	6.2	9.7	56.8	03-13-18-2	14.3	13.3	-7.3
05-13-12-1	24.4	27.8	13.9	03-14- 0-1	*	7.7	-
05-13-12-2	13.0	11.7	-10.0	03-14- 0-2	8.5	7.5	-12.0
05-13-18-1	16.4	24.6	49.8	03-14- 6-1	25.0	19.1	-23.6
05-13-18-2	10.6	11.9	12.4	03-14- 6-2	7.9	8.4	6.0
05-14- 0-1	12.7	8.9	-30.3	03-14-12-1	15.3	11.4	-25.8
05-14- 0-2	*	6.0	-	03-14-12-2	*	4.8	-
05-14- 6-1	10.1	12.6	24.6	03-14-18-1	4.5	5.9	31.9
05-14- 6-2	4.1	7.2	75.6	03-14-18-2	8.2	7.4	-9.3
05-14-12-1	13.3	12.0	-10.1	03-15- 0-1	31.6	10.5	-66.8
05-14-12-2	2.7	5.8	114.4	03-15- 0-2	17.6	18.4	4.5
05-14-18-1	*	6.1	-	03-15- 6-1	19.9	9.0	-55.0
05-14-18-2	*	4.9	-	03-15- 6-2	11.6	9.9	-14.6
05-15- 0-1	19.8	12.5	-36.8	03-15-12-1	18.6	13.9	-25.3
05-15- 0-2	4.7	11.2	138.5	03-15-12-2	15.3	10.4	-32.2
05-15- 6-1	9.8	10.5	7.2	03-15-18-1	24.5	13.5	-45.0
05-15- 6-2	12.0	12.5	3.9	03-15-18-2	10.8	15.9	46.9
05-15-12-1	18.6	14.7	-20.8	08-13- 0-1	15.4	15.2	-1.3
05-15-12-2	4.6	10.2	121.5	08-13- 0-2	*	9.5	-
05-15-18-1	17.4	14.9	-14.1	08-13- 6-1	16.3	23.3	42.7
05-15-18-2	25.2	17.6	-30.2	08-13- 6-2	15.3	15.3	.1
06-13- 0-1	12.9	14.4	11.6	08-13-12-1	13.1	25.3	92.9
06-13- 0-2	12.2	11.3	-7.8	08-13-12-2	*	7.9	-
06-13-12-1	31.5	26.9	-14.5	08-13-18-1	14.5	22.4	54.2
06-13-12-2	19.6	19.5	-.6	08-13-18-2	2.7	7.5	177.4
06-14- 0-1	10.5	11.1	5.6	08-14- 0-1	3.5	7.5	115.3
06-14- 0-2	15.3	12.6	-17.6	08-14- 0-2	*	4.6	-
06-14-12-1	16.2	10.7	-33.7	08-14- 6-1	5.9	11.3	91.7
06-14-12-2	12.9	11.4	-11.4	08-14- 6-2	*	5.1	-
06-15- 0-1	23.5	21.0	-10.9	08-14-12-1	6.0	9.7	61.5
06-15- 0-2	20.8	20.9	.3	08-14-12-2	5.0	5.1	2.9
06-15-12-1	30.2	19.3	-36.1	08-14-18-1	4.3	4.5	4.6
06-15-12-2	25.0	29.5	17.8	08-14-18-2	15.0	10.6	-29.1
03-13- 0-1	17.7	15.5	-12.5	08-15- 0-1	19.2	23.9	24.6
03-13- 0-2	10.2	11.5	12.5	08-15- 0-2	15.3	12.2	-20.1
03-13- 6-1	22.0	16.6	-24.5	08-15- 6-1	*	7.0	-
03-13- 6-2	11.1	10.3	-6.8	08-15- 6-2	4.3	5.6	30.0

*Missing value

Continued

Table 23. Continued. ($\mu g/m^3$)

One Week, All RAPS Stations

SSM

Sample	Actual[a] Mass	Calculated Mass	% Deviation	Sample	Actual Mass	Calculated Mass	% Deviation
08-15-12-1	4.2	14.5	244.5	15-13- 6-2	*	1.9	-
08-15-12-2	*	6.0	-	15-13-12-1	30.0	26.3	-12.2
08-15-18-1	13.4	12.6	-5.7	15-13-12-2	*	3.1	-
08-15-18-2	21.0	15.1	-27.9	15-14- 6-2	*	2.1	-
12-13- 0-1	5.9	13.2	123.1	15-15- 6-1	10.0	6.5	-35.1
12-13- 0-2	7.9	9.1	15.4	15-15-12-1	13.9	16.	18.1
12-13-12-1	28.4	24.7	-13.1	15-15-18-1	10.2	11.6	14.0
12-13-12-2	15.0	15.2	1.1	18-13- 0-1	9.6	9.6	.4
12-14- 0-1	7.8	8.6	9.7	18-13- 0-2	2.4	6.1	154.9
12-14- 0-2	6.7	6.3	-6.1	18-13-12-1	27.0	25.4	-6.1
12-14-12-1	9.0	8.6	-4.4	18-13-12-2	12.2	13.0	6.5
12-14-12-2	10.9	10.8	-1.4	18-14- 0-1	17.0	14.9	-12.2
12-15- 0-1	17.1	19.2	12.0	18-14- 0-2	1.0	8.6	763.6
12-15- 0-2	18.5	17.4	-5.8	18-14-12-1	7.4	7.9	7.2
12-15-12-1	18.8	19.1	1.7	18-14-12-2	4.7	8.0	71.1
12-15-12-2	18.5	16.6	-10.2	18-15-12-1	12.4	11.6	-6.7
15-13- 0-1	9.0	15.1	67.8	18-15-12-2	*	9.1	-
15-13- 6-1	20.4	20.2	-1.0				

Average Deviation = 39%[b]

Samples coded as follows: Last two digits of station number - Last two digits of day number, e.g. 13=213 - Time of day - Fraction, fine=1, coarse=2.

[a] Experimental uncertainties for stations 103, 105, 108, and 115 are $\pm 5 \mu g/m^3$ and $\pm 3 \mu g/m^3$ for stations 112, 122, and 124.

[b] Average deviation is the sum of the absolute values of the error in the mass prediction for each sample divided by the number of samples.

Table 24. Average Mass Contributions, Both Fine and Coarse Fractions. ($\mu g/m^3$)

One Week, All RAPS Stations

	SSM							
Fraction	Motor Vehicle	Soil	Limestone	Sulfate	Steel	Total	Total Observed	% Deviation
Fine	1.8	.4	0.	13.4	.1	15.7	16.0	2
Coarse	.2	3.2	6.7	.6	1.1	11.8	11.4	-4
Average	1.1	1.7	2.8	7.8	.5	13.9	14.0	1

Table 25. Results of Dimensionality Tests.

One Week, All RAPS Stations

Fine Fraction				
Factor	Eigenvalue	Chi Square	Exner	Average % Error
1	136.	291	.1620	142
2	2.04	78	.0961	94
3	.43	47	.0751	87
4	.32	28	.0547	75
5	.10	30	.0460	67
6	.08	35	.0381	64
7	.06	35	.0312	63
8	.04	36	.0250	55
9	.03	404	.0193	40

Coarse Fraction				
Factor	Eigenvalue	Chi Square	Exner	Average % Error
1	123.	90	.3118	80
2	3.46	96	.2454	75
3	2.57	66	.1810	66
4	1.41	53	.1331	58
5	.87	46	.0917	53
6	.36	44	.0677	43
7	.29	49	.0385	38
8	.06	50	.0299	38
9	.04	574	.0211	33

previous analysis of this same data divided by the days of the week but, as was the case with the data from station 112, additional factors may be resolved when the data are divided into particle-size fractions. It seems the sources contributing to the fine and coarse fractions are sufficiently different so that a factor analysis of the samples divided into particle-size fractions permits the resolution of additional sources. The zinc factor could also arise from refuse-incinerator emissions though such emissions are usually associated with a high chlorine concentration (45). The steel factor was determined from the uniqueness test for iron and found to be associated with aluminum, silicon, potassium, and calcium. Watson (12) found steel- and ferromanganese-plant emissions to be associated with these elements as part of the PACS study of the Portland, Oregon airshed. The iron factor could potentially represent iron-rich flyash emissions from coal burning power plants. Gladney (5) found iron-rich flyash particles in the size range of one to three microns at the Chalk Point electric generating station. The iron factor could also arise from entrained crustal material, though most crustal dust would be expected to be found in the coarse fraction.

The target transformation analysis of the coarse fraction indicated the presence of the two crustal sources, the first, an alumino-silicate type and the second, of limestone or cement origin. The uniqueness test indicated the presence of steel and sulfur factors with five retained factors, and a titanium source with six factors. Of the seventeen input source profiles, there was good alignment for three different crustal-like sources: soil, limestone, and coal flyash. Since there was no clear indication of the number of factors in the dimensionality tests, two separate sets of test profiles were analyzed to determine which set best represented the data. These were: soil, steel, limestone, sulfate, and flyash with five factors and soil, steel, limestone, sulfate, flyash, and paint pigment, with six factors. It is somewhat surprising for a flyash factor to align so well with the data in the coarse fraction since flyash particles would be expected to appear primarily in the fine fraction (48). It is possible that this factor represents a third crustal source, though, more information would be needed to differentiate flyash and crustal material.

The scaled source vectors that best reproduced the fine- and coarse-fraction data are listed in Table 26. In the fine fraction, the sulfur concentration of 19% in the sulfate factor is less than that expected for ammonium sulfate, though identical to that calculated for the SSM data. In the motor vehicle factor, the high aluminum and silicon values may indicate that this factor has included small amounts of crustal material not accounted for by any of the other factors. The lead concentration of 23% is much higher than that calculated in the previous analyses, though the bromine to lead ratio of 0.19 is typical for aged auto exhaust. The low sulfur concentration in the flyash/soil factor is consistent with that expected in emissions from coal burning power plants though the iron to aluminim ratio far exceeds that found by Gladney (5).

Table 26. Refined Source Profiles (mg/g).

One Week, All RAPS Stations

Fine Fraction

Element	Sulfate	Steel	Motor Vehicle	Smelter
Al	2.1	28.0	22.0	30.8
Si	3.1	33.6	19.0	15.4
S	189.0	0.0	.6	0.0
Cl	.1	9.9	18.8	14.0
K	2.0	43.0	10.6	29.7
Ca	1.5	18.0	16.0	8.8
Ti	.2	8.5	11.4	.6
Mn	0.0	7.1	.7	.8
Fe	.2	101.0	0.0	36.0
Cu	.3	1.3	3.0	19.0
Zn	0.0	2.7	6.4	202.0
Se	.1	.1	.6	.9
Br	0.0	6.9	43.0	14.0
Ba	0.0	2.9	4.7	.8
Pb	1.1	0.0	227.0	156.0

Coarse Fraction

Element	Soil	Steel	Limestone	Sulfate	Soil/ Flyash
Al	70.0	40.3	24.4	12.4	140.0
Si	294.0	0.0	131.0	0.0	150.0
S	.3	13.3	6.2	131.0	.2
Cl	.0	99.0	13.0	0.0	18.0
K	23.0	1.0	13.3	12.1	21.7
Ca	54.0	62.0	240.0	40.0	19.0
Ti	0.0	10.0	13.0	22.6	1.4
Mn	1.1	23.0	0.0	1.7	0.0
Fe	55.0	670.0	1.5	25.5	33.0
Cu	.2	.2	0.0	3.2	1.1
Zn	1.7	35.0	2.1	4.8	2.5
Se	.1	.1	.0	.0	.1
Br	.9	.6	1.8	3.4	2.0
Ba	.3	0.0	1.2	1.8	3.7
Pb	2.8	13.0	9.0	15.0	2.7

For the coarse-fraction data, reasonable fits could be made with either five or six factors. However, the scaling factor for the paint-pigment source with six retained factors resulted in a titanium concentration of around 500%, indicating the extremely small contribution of this factor. A reasonable fit to the data was achieved when the paint-pigment factor was eliminated and only five factors retained. The scaled source vectors that best produced the coarse data are listed in Table 26. The paint-pigment source that was too weak to be resolved has been absorbed into the steel and sulfate factors as manifested by the elevated titanium concentrations in these source profiles. The soil/flyash factor agrees fairly closely to that of measured coal flyash except for the somewhat higher than expected sulfur concentration. The lead and bromine concentrations are elevated in the soil, limestone, and sulfate factors. This could be a result of a small part of the fine particles being misdirected into the coarse fraction by the dichotomous samplers or by the possibility of motor vehicle and smelter emissions adhering to the surface of the larger particles and thus becoming a part of the coarse fraction. As was the case with the coarse-fraction data at station 112, the sulfate factor includes sizable concentrations of elements such as aluminum, calcium, titanium, iron, and lead. Again, this could be the result of the transformation of gaseous sulfur dioxide into sulfates on the surface of the coarse particles. To more closely examine the paint-pigment factor, a separate analysis was performed on a subset of the data consisting of twenty-eight samples that had a relatively high titanium concentration. The samples were from stations 103, 105, 106, 108, and 112, all located in the industrialized sections of the sampling area and to the north of the paint-pigment factory. A paint-pigment factor was again resolved but this time the scaling factors for some of the other sources produced physically impossible results. Again, the wide variation in the nature of the sources between the five stations seems to be inhibiting the resolution of sources. The analysis of samples from only one station, where the number of distinct sources is limited, seems to produce a superior source determination.

Tables 27 and 28 summarize the average predicted elemental concentrations for both fractions. In the fine fraction, the average percent errors for the more abundant elements, especially aluminum and silicon, are significantly larger than those calculated in the other analyses. This result is probably due to the presence of an unresolved soil or flyash component that is too weak to be accounted for by this analysis. With the exception of titanium, all the major elements in the coarse fraction are fit reasonably well. The presence of the unresolved paint-pigment factor is the probable cause for the underprediction of the titanium concentration.

Figures 5 and 6 plot the mass concentration for each source at each station. As in the previous analyses, the main contributor to the fine fraction is the sulfate aerosol. The smelter component is most important at stations 103 and 108; these stations are located to the north of the lead and zinc smelters in East St. Louis and Granite City. The contribution of the flyash/soil factor is greatest at station 105, in close proximity to two coal fired boilers. In the coarse fraction, the steel factor contributes significantly to the total sample mass at only four stations: 103, 105, 106, and 108. These stations are located in the heavily industrialized sections of

Table 27. Summary of Mass Contributions. (ng/m^3)

One Week, All RAPS Stations

	Fine Fraction						
Element	Sulfate	Steel	Motor Vehicle	Smelter	Total Predicted	Total[a] Observed	Average[b] % Error
Al	40.	41.	28.	18.	127	117 ± 5	62
Si	59.	49.	24.	9.	142	151 ± 9	64
S	3600.	0.0	0.8	0.0	3600	3560 ± 150	1
Cl	1.9	14.	24.	8.3	49	52 ± 6	169
K	38.	63.	14.	18.	132	137 ± 10	32
Ca	29.	26.	20.	5.2	81	82 ± 5	61
Ti	4.0	12.	15.	0.3	31	39 ± 7	195
Mn	0.0	10.	0.8	0.5	12	12 ± 1	119
Fe	3.8	149.	0.0	21.	173	169 ± 13	35
Cu	5.5	1.9	3.8	11.	23	24 ± 4	208
Zn	0.0	4.	8.2	120.	131	129 ± 16	23
Se	1.9	0.1	0.8	0.5	3.3	3.5 ± 0.3	88
Br	0.0	10.	55.	8.3	73	68 ± 5	45
Ba	0.0	4.2	6.0	0.5	11	11 ± 3	224
Pb	21.	0.0	290.	92.	403	407 ± 25	3

[a]Uncertainty is the standard deviation of the mean value.

[b]Average point-by-point error in predicted and measured data.

Table 28. Summary of Mass Contributions. (ng/m^3)

One Week, All RAPS Stations

	Coarse Fraction							
Element	Soil	Steel	Limestone	Sulfate	Soil/ Flyash	Total Predicted	Total[a] Observed	Average[b] % Error
Al	330.	31.	140.	20.	230.	747	753 ± 42	2
Si	1390.	0.0	740.	0.0	240.	2380	2390 ± 160	2
S	1.2	10.	35.	210.	0.3	256	259 ± 15	8
Cl	0.0	76.	74.	0.0	29.	179	193 ± 17	83
K	110.	0.7	75.	19.	35.	239	237 ± 15	19
Ca	260.	48.	1360.	64.	31.	1750	1650 ± 120	6
Ti	0.0	7.7	74.	36.	2.3	120	130 ± 21	170
Mn	5.2	18.	0.0	2.7	0.0	26	24 ± 3	53
Fe	260.	520.	8.5	41.	53.	880	880 ± 80	2
Cu	0.7	0.1	0.0	5.1	1.8	7.7	7.8 ± 0.7	135
Zn	8.1	27.	12.	7.7	4.0	59	52 ± 5	110
Se	0.2	0.1	0.0	0.0	0.2	0.5	0.4 ± 0.03	90
Br	4.1	0.4	10.	5.4	3.2	23	21 ± 2	76
Ba	1.3	0.0	6.8	2.9	6.0	17	17 ± 2	166
Pb	13.	10.	51.	24.	4.4	103	100 ± 9	71

[a]Uncertainty is the standard deviation of the mean value.

[b]Average point-by-point error in predicted and measured data.

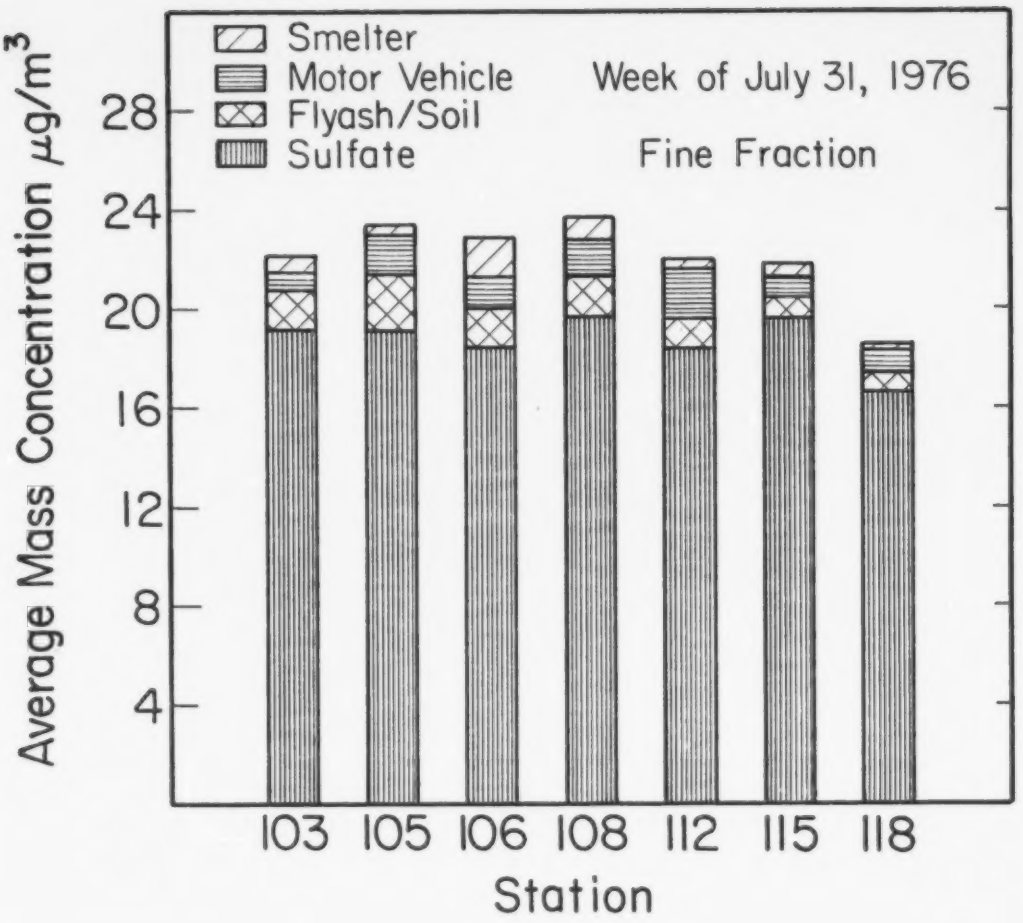

Figure 5. A comparison of the calculated mass concentrations of the four source components in the fine-fraction data from all RAPS stations. These samples are from the week beginning July 31, 1976.

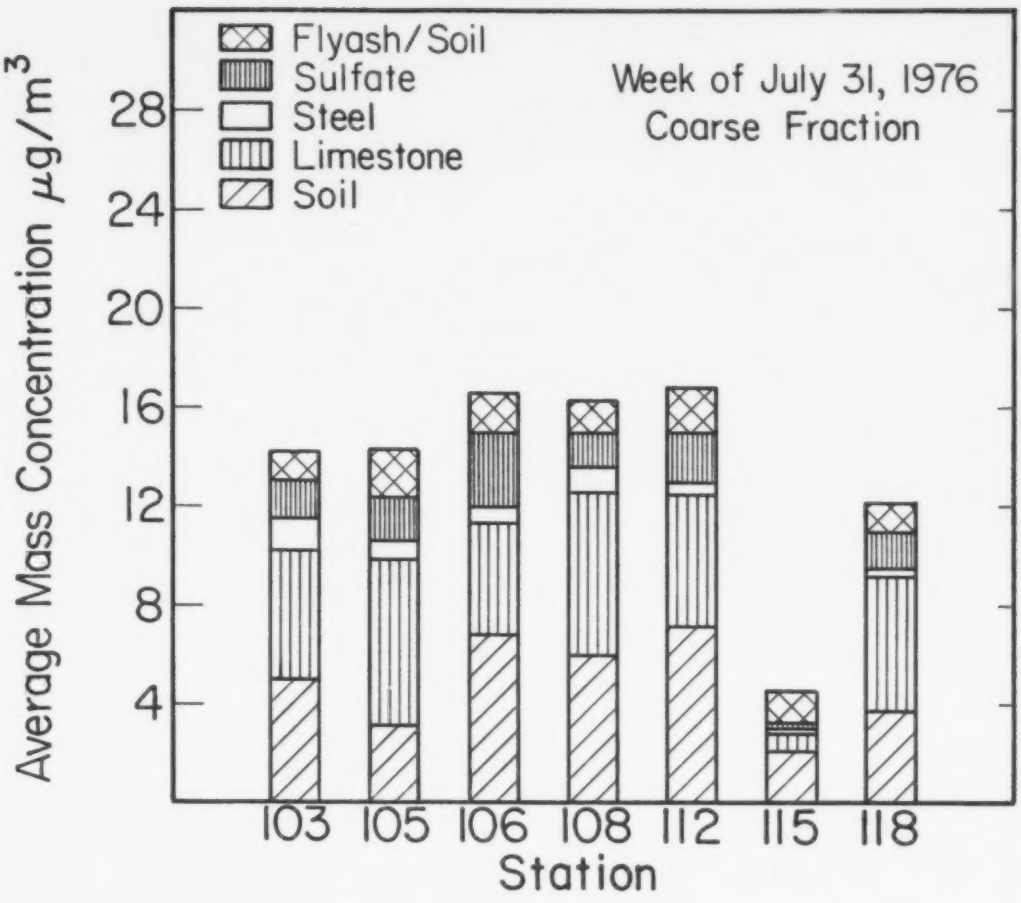

Figure 6. A comparison of the calculated mass concentrations of the five source components in the coarse-fraction data from all RAPS stations. These samples are from the week beginning July 31, 1976.

the sampling area and in close proximity to the iron works and foundries. A comparison of the predicted and total measured sample masses are given in Tables 29 and 30. The average deviations in the mass predictions are 32% in the fine fraction and 34% in the coarse; slightly better than that calculated for the SSM data.

Another problem with the quality of this data set is exemplified by the measured mass of the sample from station 108, day 218, time zero, in the fine fraction (08-18- 0-1). The measured mass is $8.6 \pm 5 \mu g/m^3$ while the calculated mass is $51.2 \mu g/m^3$, an error of nearly 500%! However, the sum of the mass concentrations of the 27 elements that were determined for this sample is nearly $12 \mu g/m^3$. If it is assumed that these elements are present as oxides then the sample mass should approach $30 \mu g/m^3$. Clearly, there are problems with the determinations of the total sample mass in this version of the RAPS data.

Figure 7 summarizes the average mass contribution of each source for the fine and coarse fractions. The predicted motor vehicle concentration of 6% is lower than in the analysis of the SSM data. With the addition of the not previously resolved smelter factor, the measured lead concentration is now apportioned among two factors. Motor vehicle emissions account for about 72% of the lead concentration while smelters contribute about 23%. In the coarse fraction, the two crustal components account for 70% of the total mass. The soil/flyash component contributes an additional 10%.

If the concentration of carbon in motor vehicle emissions is again assumed to be 500 mg/g, then the ambient carbon concentration from this source would be about $700 ng/m^3$. However, the large average percent error in the measured versus predicted sample masses may indicate that the undetermined elements do not correlate very well with the analyzed elements. Attempts to estimate the contribution of the unmeasured elements would be difficult and the reliability of the results highly uncertain.

Table 29. Predicted vs. Measured Sample Mass ($\mu g/m^3$)

One Week, All RAPS Stations

Fine Fraction

Sample	Actual[a] Mass	Calculated Mass	% Deviation	Sample	Actual Mass	Calculated Mass	% Deviation
05-16- 0-1	21.1	19.5	-7.5	18-17-12-1	25.1	24.2	-3.8
05-16- 6-1	24.6	29.5	19.8	05-18- 0-1	26.5	32.7	23.5
05-16-12-1	37.8	32.5	-14.0	05-18- 6-1	42.6	49.1	15.1
05-16-18-1	30.8	25.1	-18.6	05-18-12-1	35.8	37.5	4.7
05-17- 0-1	30.2	27.2	-10.1	05-18-18-1	36.5	32.8	-10.2
05-17- 6-1	40.7	41.5	2.0	05-19- 0-1	15.0	18.9	25.9
05-17-12-1	23.7	30.6	29.2	05-19- 6-1	17.3	17.5	1.1
05-17-18-1	23.0	24.3	5.7	05-19-12-1	22.9	18.8	-18.1
06-16- 0-1	21.2	19.1	-10.0	05-19-18-1	33.9	32.7	-3.7
06-16-12-1	35.7	32.3	-9.5	06-18-12-1	42.8	39.4	-8.0
06-17- 0-1	31.4	31.2	-.8	06-19- 0-1	17.0	14.0	-17.5
06-17-12-1	29.9	31.3	4.6	06-19-12-1	27.3	25.6	-6.2
03-16- 0-1	19.1	15.3	-20.0	03-18- 0-1	43.0	36.2	-15.8
03-16- 6-1	21.5	14.3	-33.7	03-18- 6-1	43.8	48.4	10.4
03-16-12-1	36.6	29.5	-19.3	03-18-12-1	38.5	38.6	.3
03-17-12-1	35.6	34.5	-3.1	03-18-18-1	44.1	32.7	-25.8
03-17-18-1	37.5	30.2	-19.4	03-19- 0-1	50.4	22.3	-55.7
08-16- 0-1	8.8	9.1	3.2	03-19- 6-1	20.5	15.8	-23.1
08-16- 6-1	12.4	14.2	14.8	03-19-12-1	29.6	30.6	3.2
08-16-12-1	21.3	28.2	32.6	03-19-18-1	26.3	26.6	1.0
08-16-18-1	27.7	27.8	.4	08-18- 0-1	8.6	51.2	495.7+
08-17- 0-1	26.8	30.2	12.8	08-18- 6-1	*	42.5	-
08-17- 6-1	41.9	44.4	5.9	08-18-12-1	*	37.6	-
08-17-12-1	30.3	34.9	15.1	08-18-18-1	38.4	37.6	-2.1
08-17-18-1	132.8	42.8	-67.8	08-19- 0-1	16.5	14.8	-10.1
12-16- 0-1	22.8	23.4	2.8	08-19- 6-1	18.7	16.9	-9.7
12-16-12-1	38.4	34.7	-9.7	08-19-12-1	*	17.5	-
12-17- 0-1	32.7	30.6	-6.5	08-19-18-1	36.8	31.6	-14.2
12-17-12-1	31.1	29.5	-5.1	12-18- 0-1	30.2	31.5	4.3
15-16- 0-1	9.0	7.5	-17.1	12-19-12-1	19.5	21.8	11.7
15-16- 6-1	2.8	12.5	346.4	15-18- 0-1	16.1	30.1	86.6
15-16-12-1	15.0	16.6	10.4	15-18-12-1	30.5	36.4	19.4
15-16-18-1	23.9	24.8	3.9	15-18-18-1	31.0	34.9	12.6
15-17- 0-1	7.2	19.6	171.7	15-19- 0-1	12.7	22.7	79.0
15-17- 6-1	38.2	41.6	9.0	15-19- 6-1	8.8	15.2	72.8
15-17-12-1	24.7	32.7	32.4	15-19-12-1	*	11.8	-
15-17-18-1	14.9	30.0	101.0	15-19-18-1	11.9	21.6	81.3
18-16- 0-1	16.6	10.9	-34.5	18-18- 0-1	29.1	30.8	5.9
18-16-12-1	28.1	24.5	-12.9	18-18-12-1	27.0	27.0	-.0
18-17- 0-1	18.9	23.6	24.8	18-19- 0-1	8.9	11.9	33.7

*Missing value +see note in text Continued

Table 29. Continued ($\mu g/m^3$)

One Week, All RAPS Stations

Fine fraction

Sample	Actual[a] Mass	Calculated Mass	% Deviation	Sample	Actual Mass	Calculated Mass	% Deviation
05-13- 0-1	11.0	17.2	56.4	08-13- 0-1	15.4	16.5	7.3
05-13- 6-1	15.8	16.0	1.5	08-13- 6-1	16.3	23.5	44.3
05-13-12-1	24.4	27.8	14.1	08-13-12-1	13.1	25.2	92.6
05-13-18-1	16.4	25.1	53.2	08-13-18-1	14.5	22.4	54.4
05-14- 0-1	12.7	9.3	-27.0	08-14- 0-1	3.5	7.5	114.5
05-14- 6-1	10.1	12.9	27.6	08-14- 6-1	5.9	11.4	93.7
05-14-12-1	13.3	12.5	-6.3	08-14-12-1	6.0	9.9	65.0
05-14-18-1	*	5.9	-	08-14-18-1	4.3	4.5	3.6
05-15- 0-1	19.8	13.0	-34.3	08-15- 0-1	19.2	19.1	-.6
05-15- 6-1	9.8	11.7	19.0	08-15- 6-1	*	6.8	-
05-15-12-1	18.6	15.8	-15.2	08-15-12-1	4.2	15.0	256.7
05-15-18-1	17.4	17.9	2.6	08-15-18-1	13.4	12.7	-5.4
06-13- 0-1	12.9	14.1	9.4	12-13- 0-1	5.9	12.4	110.0
06-13-12-1	31.5	26.6	-15.4	12-13-12-1	28.4	24.7	-12.9
06-14- 0-1	10.5	11.6	10.2	12-14- 0-1	7.8	8.5	9.6
06-14-12-1	16.2	11.5	-29.2	12-14-12-1	9.0	8.5	-5.2
06-15- 0-1	23.5	21.1	-10.0	12-15- 0-1	17.1	19.1	11.5
06-15-12-1	30.5	20.1	-34.0	12-15-12-1	18.8	19.3	2.8
03-13- 0-1	17.7	16.3	-8.0	15-13- 0-1	9.0	15.2	69.3
03-13- 6-1	22.0	16.8	-23.6	15-13- 6-1	20.4	21.2	3.7
03-13-12-1	26.9	27.4	2.0	15-13-12-1	30.0	26.5	-11.7
03-13-18-1	27.2	27.2	0.0	15-15- 6-1	10.0	6.8	-32.1
03-14- 0-1	*	8.1	-	15-15-12-1	13.9	17.2	23.6
03-14- 6-1	25.0	19.9	-20.4	15-15-18-1	10.2	12.3	20.6
03-14-12-1	15.3	12.0	-21.6	18-13- 0-1	9.6	8.9	-7.0
03-14-18-1	4.5	5.9	31.8	18-13-12-1	27.0	25.5	-5.7
03-15- 0-1	31.6	11.1	-65.0	18-14- 0-1	17.0	15.8	-7.2
03-15- 6-1	19.9	9.3	-53.2	18-14-12-1	7.4	8.2	10.4
03-15-12-1	18.6	14.6	-21.8	18-15-12-1	12.4	11.9	-4.2
03-15-18-1	24.5	13.3	-45.6				

Average Deviation = 31.7%[b]

Samples coded as follows: Last two digits of station number - Last two digits of day number, e.g. 13 = day 213 - Time of day - Fraction, fine = 1, coarse = 2.

[a]Experimental uncertainties for stations 103, 105, 108, and 115 are $\pm$ 5$\mu g/m^3$ and $\pm$ 3$\mu g/m^3$ for stations 112, 122, and 124.

[b]Average deviation is the sum of the absolute values of the error in the mass prediction for each sample divided by the number of samples.

Table 30. Predicted vs. Measured Sample Mass ($\mu g/m^3$).

One Week, All RAPS Stations

Coarse Fraction

Sample	Actual[a] Mass	Calculated Mass	% Deviation	Sample	Actual Mass	Calculated Mass	% Deviation
05-16- 0-2	10.8	14.7	35.9	05-18- 6-2	32.0	31.7	-1.0
05-16- 6-2	40.4	32.7	-19.2	05-18-12-2	10.1	18.4	82.2
05-16-12-2	25.1	23.8	-5.3	05-18-18-2	8.5	12.7	49.4
05-16-18-2	11.1	16.3	46.9	05-19- 0-2	11.3	9.9	-12.8
05-17- 0-2	25.6	26.3	2.6	05-19- 6-2	17.2	14.3	-16.9
05-17- 6-2	27.6	28.2	2.0	05-19-12-2	*	12.6	-
05-17-12-2	13.3	17.5	31.8	05-19-18-2	8.3	12.2	46.6
05-17-18-2	12.7	15.4	21.0	06-18-12-2	*	27.6	-
06-16- 0-2	33.8	29.4	-13.1	06-19- 0-2	17.6	13.0	-26.3
06-16-12-2	32.5	25.9	-20.4	06-19-12-2	16.0	12.0	-24.8
06-17- 0-2	30.6	31.7	3.7	03-18- 0-2	22.0	25.5	15.7
06-17-12-2	33.0	29.0	-12.1	03-18- 6-2	25.8	26.8	3.9
03-16- 0-2	28.4	34.2	20.5	03-18-12-2	28.2	28.0	-.9
03-16- 6-2	25.7	25.1	-2.5	03-18-18-2	14.9	17.8	19.7
03-16-12-2	31.3	20.5	-34.4	03-19- 0-2	8.9	8.2	-7.4
03-17-12-2	*	23.1	-	03-19- 6-2	1.7	6.3	269.9
03-17-18-2	30.9	24.0	-22.4	03-19-12-2	16.6	7.8	-53.1
08-16- 0-2	11.1	11.6	4.5	03-19-18-2	17.3	8.5	-50.7
08-16- 6-2	13.9	13.8	-1.1	08-18- 0-2	*	31.5	-
08-16-12-2	21.9	16.7	-23.8	08-18- 6-2	28.5	32.1	12.6
08-16-18-2	33.1	34.1	2.9	08-18-12-2	11.6	22.3	92.2
08-17- 0-2	43.8	42.4	-3.2	08-18-18-2	15.3	17.3	13.1
08-17- 6-2	73.2	65.5	-10.6	08-19- 0-2	*	4.0	-
08-17-12-2	27.5	27.1	-1.5	08-19- 6-2	6.9	9.8	41.4
08-17-18-2	16.7	24.0	43.8	08-19-12-2	*	4.1	-
12-16- 0-2	38.0	35.4	-6.8	08-19-18-2	*	5.1	-
12-16-12-2	30.5	23.6	-22.7	12-18- 0-2	23.7	21.5	-9.1
12-17- 0-2	31.7	26.3	-17.1	12-19-12-2	6.1	8.2	34.4
12-17-12-2	24.3	21.0	-13.4	15-18- 6-2	*	7.9	-
15-16- 0-2	*	2.2	-	15-18-12-2	*	8.8	-
15-16- 6-2	*	4.8	-	15-18-18-2	*	5.4	-
15-16-12-2	*	4.7	-	15-19- 0-2	*	.8	-
15-16-18-2	*	5.0	-	15-19-18-2	*	1.0	-
15-17- 6-2	*	8.0	-	18-18- 0-2	20.3	19.0	-6.4
15-17-12-2	*	4.6	-	18-18-12-2	13.6	14.1	3.4
18-16- 0-2	15.8	13.5	-14.6	18-19- 0-2	6.1	6.4	4.9
18-16-12-2	21.4	19.4	-9.3	05-13- 0-2	6.9	8.8	27.8
18-17- 0-2	21.0	21.2	1.1	05-13- 6-2	6.2	9.3	49.7
18-17-12-2	9.8	12.6	28.6	05-13-12-2	13.0	10.7	-17.9
05-18- 0-2	10.9	15.7	43.7	05-13-18-2	10.6	10.6	-.3

*Missing value

Continued

Table 30. Continued ($\mu g/m^3$)

One Week, All RAPS Stations

Coarse Fraction

Sample	Actual[a] Mass	Calculated Mass	% Deviation	Sample	Actual Mass	Calculated Mass	% Deviation
05-14- 0-2	*	5.2	-	08-13- 0-2	*	8.2	-
05-14- 6-2	4.1	6.9	68.0	08-13- 6-2	15.3	15.2	-.5
05-14-12-2	2.7	4.8	77.9	08-13-12-2	*	7.6	-
05-14-18-2	*	4.2	-	08-13-18-2	2.7	7.1	161.3
05-15- 0-2	4.7	9.2	95.3	08-14- 0-2	*	4.1	-
05-15- 6-2	12.0	10.4	-13.3	08-14- 6-2	*	5.2	-
05-15-12-2	4.6	8.8	91.0	08-14-12-2	5.0	4.4	-11.8
05-15-18-2	25.2	14.9	-41.0	08-14-18-2	15.0	9.1	-39.1
06-13- 0-2	12.2	10.0	-18.3	08-15- 0-2	15.3	10.6	-31.0
06-13-12-2	19.6	17.6	-10.5	08-15- 6-2	4.3	4.7	9.7
06-14- 0-2	15.3	11.4	-25.3	08-15-12-2	*	5.6	-
06-14-12-2	12.9	9.9	-23.2	08-15-18-2	21.0	12.6	-39.9
06-15- 0-2	20.8	16.6	-20.4	12-13- 0-2	7.9	7.8	-1.2
06-15-12-2	25.0	25.9	3.5	12-13-12-2	15.0	13.5	-10.3
03-13- 0-2	10.2	10.9	6.9	12-14- 0-2	6.7	5.8	-14.1
03-13- 6-2	11.1	9.6	-13.1	12-14-12-2	10.9	8.9	-18.7
03-13-12-2	13.7	10.3	-24.8	12-15- 0-2	18.5	15.1	-18.4
03-13-18-2	14.3	11.0	-23.1	12-15-12-2	18.5	13.8	-25.6
03-14- 0-2	8.5	6.4	-24.7	15-13- 6-2	*	2.2	-
03-14- 6-2	7.9	7.7	-2.2	15-13-12-2	*	3.6	-
03-14-12-2	*	4.2	-	15-14- 6-2	*	2.7	-
03-14-18-2	8.2	6.4	-22.1	18-13- 0-2	2.4	5.4	125.1
03-15- 0-2	17.6	13.7	-22.2	18-13-12-2	12.2	12.4	1.6
03-15- 6-2	11.6	9.2	-21.1	18-14- 0-2	1.0	7.3	634.8
03-15-12-2	15.3	8.9	-41.6	18-14-12-2	4.7	6.9	46.6
03-15-18-2	10.8	14.0	29.2	18-15-12-2	*	7.6	-

Average Deviation = 33.8%[b]

[a] Experimental uncertainties for stations 103, 105, 108, and 115 are $\pm$ 5$\mu g/m^3$ and $\pm$ 3$\mu g/m^3$ for stations 112, 122, and 124.

[b] Average deviation is the sum of the absolute values of the error in the mass prediction for each sample divided by the number of samples.

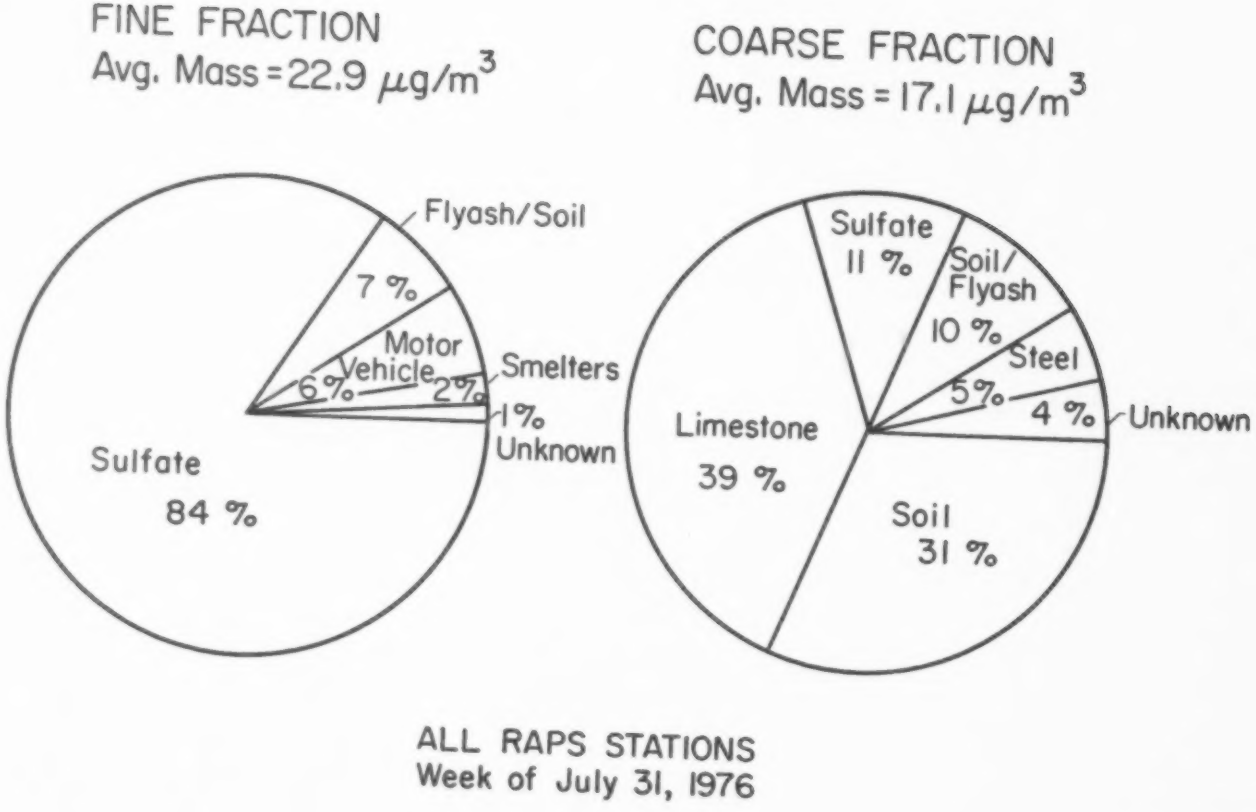

Figure 7. Average percent contribution of each source to the total average mass. The data are the fine- and coarse-fraction samples from all RAPS stations for the seven days beginning July 31, 1976.

REFERENCES

1. Miller, M.S., S.K. Friedlander, and G.M. Hidy. A Chemical Element Balance for the Pasadena Aerosol. J. Colloid Interface Sci., 39:165-176, 1972.

2. Heindryckx, R. and R. Dams. Continental, Marine, and Anthropogenic Contributions of the Aerosol of an Individual Zone. J. Radioanal. Chem., 19:339-349, 1974.

3. Bogen, J. Trace Elements in the Atmospheric Aerosol in the Heidelberg Area Measured by Instrumental Neutron Activation Analysis. Atmospheric Environ., 7:1117-1125, 1973.

4. Gatz, D.F. Relative Contributions of Different Sources of Urban Aerosols: Application of a New Estimation Method to Multiple Sites in Chicago. Atmospheric Environ., 9:1-18, 1975.

5. Gladney, E.S. Trace Elemental Emissions From Coal-Fired Power Plants: A Study of the Chalk Point Electric Generating Station. PhD Thesis, University of Maryland, College Park, Maryland, 1974.

6. Mroz, E.J. The Study of the Elemental Composition of Particulate Emissions From an Oil-Fired Power Plant. PhD Thesis, University of Maryland, College Park, Maryland, 1976.

7. Greenberg, R.R. A Study of Trace Elements Emitted on Particles From Municipal Incinerators. PhD Thesis, University of Maryland, College Park, Maryland, 1976.

8. Ondov, J.M. A Study of Trace Elements On Particulates From Motor Vehicles. PhD Thesis, University of Maryland, College Park, Maryland, 1974.

9. Thomae, S.C. Size and Composition of Atmospheric Particles in Rural Areas Near Washington D.C. PhD Thesis, University of Maryland, College Park, Maryland, 1977.

10. Kowalczyk, G.S. Concentration and Sources of Elements on Washington, D.C. Area Atmospheric Particles. PhD Thesis, University of Maryland, College Park, Maryland, 1979.

11. Dzubay, T.G. Chemical Element Balance Method Applied to Dichotomous Sampler Data. Annals of the New York Academy of Sciences, 338:126-144,1980

12. Watson, J.G., Jr. Chemical Element Balance Receptor Methodology For the Sources of Fine and Total Suspended Particulate Matter in Portland, Oregon. PhD Thesis, Oregon Graduate Center, Beaverton, OR, 1979.

13. Kowalczyk, J.F., J.E. Core, and J.A. Cooper. The True Sources of Portland's Suspended Particulate. Presented to the Pacific Northwest International Section, Air Pollution Control Association, November 1979, Paper Number 79 - 10.5.

14. Hopke, P.K., E.S. Gladney, G.E. Gordon, W.H. Zoller, and A.G. Jones. The Use of Multivariate Analysis to Identify Sources of Selected Elements in the Boston Urban Aerosol. Atmospheric Environ., 10:1015-1025, 1976.

15. Gaarenstroom, P.D., S.P. Perone, and J.L. Moyers. Application of Pattern Recognition and Factor Analysis for Characterization of Atmospheric Particulate Composition in Southwest Desert Atmosphere. Environ. Sci. Technol., 11:795-800, 1977.

16. Gatz, D.F. Identification of Aerosol Sources in the St. Louis Area Using Factor Analysis. J. Appl. Met., 17:600-608, 1978.

17. Hopke, P.K., R.E. Lamb, and D.F. Natusch. Multielemental Characterization of Urban Roadway Dust. Environ. Sci. Technol., 14:164-172, 1980.

18. Alpert, D.J. and P.K. Hopke. Applicability of Factor Analysis to the Study of Source Components in Environmental Systems. In: Proceedings of the National Conference on Quality Assurance of Environmental Measurements, Denver, CO, 1978.

19. Hopke, P.K. Source Identification and Resolution Through Application of Factor and Cluster Analysis. Annals of the N.Y. Academy of Science, 338:103-105, 1980.

20. Alpert, D.J. Quantitative Apportionment of Urban Aerosol Mass by Factor Analysis. PhD Thesis, University of Illinois, Urbana, Illinois, 1980.

21. Alpert, D.J. and P.K. Hopke. A Quantitative Determination of Sources in the Boston Urban Aerosol. Atmospheric Environ., (in press).

22. Weiner, P.H., E.R. Malinowski, and A.R. Levinstone. Factor Analysis of Solvent Shifts in Proton Magnetic Resonance. J. Phys. Chem., 74:4537-4542, 1970.

23. Rozett, R.W. and E.M. Petersen. Methods of Factor Analysis of Mass Spectra. Anal. Chem., 47:1301-1308, 1975.

24. Exner, O. Additive Physical Properties. Collection of Czech. Chem. Commun., 31:3222-3253, 1966.

25. Harmon, H.H., Modern Factor Analysis, 3rd Ed., Revised. The University of Chicago Press, Chicago, IL, 1976.

26. Clifford, A.A. Multivariate Error Analysis. Applied Sciences Publishers, Ltd., London, 1973.

27. Bevington, P.R. Data Reduction and Error Analysis for the Physical Sciences. McGraw-Hill Book Company, New York, NY, 1969.

28. Alpert, D.J., B.A. Roscoe, and P.K. Hopke. FANTASIA - Factor Analysis to Apportion Sources in Aerosols - A Computer Code. IES Staff Paper no. 11. Institute for Environmental Studies, University of Illinois, Urbana, IL, 1980.

29. Malinowski, E.R., D.G. Howery, P.H. Weiner, J.M. Sorka, P.T. Funke, R.B. Swizer, and A.R. Levinstone. FACTANL - Target Transformation Factor Analysis, Program 320, Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN, 1976.

30. Nelson, E. Regional Air Pollution Study: Dichotomous Aerosol Sampling System. EPA-297 310, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1979.

31. Goulding, F.S., J.M. Jaklevic, and B.W. Loo. Aerosol Analysis for the Regional Air Pollution Study -- Interim Report. EPA-600/4-78-034, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1978.

32. Daisey, J.M., I. Hawryluk, T.J. Kneip, and F. Mukai. Mutagenic Activity in Organic Fractions of Airborne Particulate Matter. In Proceedings of the Conference on Carbonaceous Particles in the Atmosphere. Lawrence Berkeley Laboratory Report LBL-9037, CONF-7803101, UC-11, 1978.

33. Kaden, D.A. and W.G. Thilly. Mutagenic Activity in Fossil Fuel Combustion Products. In Proceedings of the Conference on Carbonaceous Particles in the Atmosphere. Lawrence Berkeley Laboratory Report LBL-9037, CONF-7803101, UC-11, 1978.

34. Lewis, C.W. and E.S. Macias. Composition of Size-Fractionated Aerosol in Charleston, West Virginia. Atmospheric Environ., 14:185-194, 1980.

35. Lodge, J.P., G.S. Bien, and H.E. Suess. The Carbon-14 Contents of Urban Airborne Particulate Matter. Int. J. Air Poll., 22:309-312, 1960.

36. Currie, L.A. and S.M. Kunen, K.J. Voorhees, R.B. Murphy, and W.F. Koch. Analysis of Carbonaceous Particulates and Characterization of Their Sources by Low-Level Radiocarbon Counting and Pyrolysis/Gas Chromatography/Mass Spectrometry. In Proceedings of the Conference on Carbonaceous Particles in the Atmosphere. Lawrence Berkeley Laboratory Report LBL-9037, CONF-7803101, UC-11, 1978.

37. Mason, B. Principles of Geochemistry, 3rd Ed. John Wiley & Sons, Inc., New York, NY, 1966.

38. Dybczynski, R., A. Tugsavul, and O. Suschny. Report on the Intercomparison Run Soil-5 for the Determination of Trace Elements in Soil. International Atomic Laboratory Seiberdorf, (unpublished report to participants), 1978.

39. Friedlander, S.K. Chemical Element Balances and Identification of Air Pollution Sources. Environ. Sci. Technol., 7:235-240, 1973.

40. Vinogradov, A.P. The Geochemistry of Rare and Dispersed Chemical Elements in Soils, 2nd Ed. Consultants Bureau, Inc., New York, NY, 1959.

41. Taylor, S.R. Abundance of Chemical Elements in the Continental Crust: A New Table. Geochem. Cosmochem. Acta, 28(1273-1285), 1964.

42. Ondov, J.M., W.H. Zoller, I. Olmez, N.K. Aras, G.E. Gordon, L.A. Rancetelli, K.H. Filby, K.R. Shan, and R.C. Ragaini. Elemental Concentrations in the NBS Environmental Coal and Flyash Standard Reference Material. Anal. Chem., 47:1102-1109, 1975.

43. Rheingrover, S.W. A Statistical Model for Titanium Pollution Transport and Dispersion in the Atmosphere of St. Louis. M.S Thesis, Florida State University, Tallahassee, Florida, 1977.

44. Dzubay, T.G., R.K. Stevens, and L.W. Richards. Composition of Aerosols Over Los Angeles Freeways. Atmospheric Environ., 13:653-659, 1979.

45. Greenberg, R.R., G.E. Gordon, and W.H. Zoller. Composition of Particles from the Nicosia Municipal Incinerator. Environ. Sci. Technol., 12:1329-1332, 1978.

46. Pierson, W.R. Particulate Organic Matter and Total Carbon From Vehicles on the Road. In Proceedings of the Conference on Carbonaceous Particles in the Atmosphere. Lawrence Berkeley Laboratory Report LBL-9037, CONF-7803101, UC-11, 1978.

47. Fisher, G.L., C.E. Chrisp, and T.L. Hayes. Carbonaceous Particles in Coal Flyash. In Proceedings of the Conference on Carbonaceous Particles in the Atmosphere. Lawrence Berkeley Laboratory Report LBL-9037, CONF-7803101, UC-11, 1978.

48. Ondov, J.M., R.C. Ragaini, and A.H. Biermann. Elemental Particle-Size Emissions for Coal-Fired Power Plants: Use of an Inertial Cascade Impactor. Atmospheric Environ., 12:1175-1185, 1978.

Appendix

The difference between the rotated column of the A matrix and the input test vector b is given by epsilon

$$\varepsilon = Ar - b$$

In a least squares fit, the quantity to be minimized is ε^2 given by

$$\varepsilon^2 = (Ar - b)^t(Ar - b)$$

rearranging yields

$$\varepsilon^2 = (r^tA^t - b^t)(Ar - b)$$

$$\varepsilon^2 = r^tA^tAr - r^tA^tb - b^tAr + b^tb$$

The third term in this equation is a scaler quantity and thus equal to its transpose

$$\varepsilon^2 = r^tA^tAr - 2r^tA^tb - b^tb$$

taking the derivative and setting it equal to zero

$$\frac{\partial \varepsilon^2}{\partial r} = 0 = 2A^tAr - 2A^tb$$

rearranging

$$r = (A^tA)^{-1}A^tb$$

comparing this equation with equations 6 and 7 leads to

$$r = (A)^{-1}A^tb$$